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Electrochemical Studies on Peroxo Heteroligand Vanadates (V) in Aqueous Solution

David J. Mayonado
College of William & Mary - Arts & Sciences

ELECTROCHEMICAL STUDIES ON PEROXO HETEROLIGAND VANADATES (V) IN AQUEOUS SOLUTION

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APPROVAL SHEET

This thesis is submitted in partial fulfillment of the requirement for the degree of

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David J. Mayonado

David J. Mayonado, Author

Approved, June 1984

Cirila Djordjevic, Ph. D., Chemistry

William H. Bunnelle

William H. Bunnelle, Ph. D., Chemistry

David W. Thompson, Ph. D., Chemistry

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ABSTRACT

Cyclic voltammetry and potentiometric titrations were used to characterize electrochemical behavior of peroxo heteroligand vanadium(V) complexes in various electrolytic media. Peak positions, currents, and relationships of anodic and cathodic peak potentials were used to determine the electrochemical behavior of the systems. Comparison of the electroactive species in the solutions of the crystalline compounds with the solutions obtained by mixing the components of the compounds were made to determine differences in the two systems. Results show that under all conditions, irreversible processes occur on a glassy carbon electrode. The following compounds were studied: $(NH_4)_4[O\ VO(O_2)_2]$, $M^I_3[VO(O_2)_2C_2O_4]$, and $M^I[VO(O_2)L]$, L=malate, citrate, tartrate, NTA and EDTA. Electrochemical behavior depends upon the type of the complex and the type of inert electrolyte used.

INTRODUCTION

Vanadium is one of the very interesting elements to study electrochemistry. In aqueous solution, the existence of several oxidation states, the possibility of polymerization and hydrolysis result in complex electrochemistry, complicated further in the presence of ligands which form stable complexes with vanadium. Such situations discourage many electrochemists, and there are few reports on such systems in the literature. Nonaqueous solvents are more popular[1,2] since they avoid hydrolysis and generally polymerization. However, special interest in vanadium lies basically in the fact that this metal has recently been recognized as an essential element for mammals,[3] but its functions are unknown.[4,5,6] Chemistry of life proceeds in aqueous solutions. We have therefore decided to start a systematic study of aqueous electrochemistry of vanadium in the presence of heteroligands relavent to the biochemistry of vanadium.

This thesis describes our studies and is presented in five sections. The literature survey gives a broad overview of the basic chemistry of vanadium including its behavior in aqueous solution, electrochemistry, and reactions with peroxide. Also included is a review on potentiometric

titrations, cyclic voltammetry, and the electrochemistry of the peroxo group.

In the experimental section, the electrochemistry of various oxoperoxovanadium (V) compounds and analogous vanadium(V) solutions is studied through the use of automatic potentiometric titrations and cyclic voltammetry. Descriptions and pertinent observations of the experimental work are included.

The results of the study along with discussions of their significance are summarized in Section 4. Section 5 follows with a brief summary of general conclusions from the study.

2.1 CHEMISTRY OF VANADIUM

Vandium, named after Vanadis the legendary Norse goddess of beauty in recognition of the beautiful colors of its derivatives, is a greyish-silver metal that is soft and ductile in its pure form. These physical properties allow commercial utilization of vanadium in the production of alloy steels and cast iron to which it lends ductility and shock resistance.[7]

At ordinary temperatures, vanadium has good corrosion resistance to salt water and is relatively inert towards oxygen, nitrogen, and hydrogen. It is also resistant to attack by hydrochloric or dilute sulfuric acid and to alkali solutions. It is, however, reactive towards concentrated sulfuric acid, nitric acid and hydroflouric acids.[8]

At high temperatures, vanadium combines with most non-metals and since its atomic radius of $1.36\overset{o}{A}$ is not appreciably different from that of a large number of other elements, a variety of solid solutions with other elements is possible.[9]

Vanadium is a typical transition element with the ground state configuration $3d^3 4s^2$. It therefore, displays

a number of oxidation states ranging from the expected group state of (V) down to (0). The oxidation state (0) and (I) are rare so their chemistry will only briefly be presented.

The oxidation states (II) through (V) are more common. They are found in aqueous solutions as well as solid compounds. They form compounds with halogens, oxides, oxohalides and form a host of complexes. The halides and oxohalides are excellent sources of vanadium for other compounds and are used commercially as catalysts, particularly in the field of olefin polymerization.[8]

A brief survey of the chemistry of various vanadium oxidation states is given below.

$\underline{V(0)d^5}$

V(0) occurs rarely and only in compounds where the ligand field can stablize the low oxidation state by drawing electron density away from the metal. An example is $V(CO)_6$. The π-antibonding orbitals origination from the (CO) triple bond overlap with d orbitals from the metal allowing the delocalization of electron density from the metal to the empty orbitals.[7]

V(I)d^4

V(I) is even more rare than V(0) and also occurs only in compounds where the low oxidation state is stablized by back-bonding. Examples are h^5-$C_5H_5V(CO)_4$ and $[Vphen_3]+$.

V(II)d^3

The chemistry of V(II) is not well established. There is however, a multitude of V(II) compounds that have been characterized. In this oxidation state, the element resembles chromium but is more readily oxidized.[9] V(II) compounds are so easily oxidized that many are used as reducing agents.

Halide compounds of V(II) include VF_2, VCl_2, VBr_2 and VI_2. They all are colored, paramagnetic solids that are hygroscopic and strongly reducing. VF_2 has the tetragonal crystal structure while the remaining halides have the hexagonal structure. In water, all V(II) halides form the $V(H_2O)_6^{2+}$ ion which may form crystalline salts.[9]

The oxide of V(II) is vanadium monoxide (VO). It is a grey, metallic powder that is paramagnetic and a conductor of electricity. It has a crystal structure similar to that of sodium chloride and tends to be non-stoichiometric, being obtainable with anywhere from 45 to 55 atom % oxygen.[7]

V(III)d^2

Vanadium in oxidation state (III) forms the halides VF_3, VCI_3, VBr_3 and VI_3. They all are colored, crystalline solids, all of which are polymeric involving six-coordinate vanadium atoms. VF_3 has rhombohedral crystal structure while the others are hexagonal. All the trihalides except VF_3 are hygroscopic, forming the $V(H_2O)_6^{3+}$ ion in solution, and they are readily oxidized by air. The triflouride is insoluble in common organic solvents and almost insoluble in water. It is less easily oxidized than the other trihalides.[9]

Two oxyhalides of V(III), VOCI and VOBr, have been characterized. Both have the orthorhombic crystalline structure but little more is known of these compounds.[9]

The oxide of V(III) is V_2O_3. This black solid has rhombohedral crystalline structure. It is oxidized by air to VO_2 and may be reduced to the metal by calcium hydride.[10]

V(III) forms a large number of complexes including not only monodentate ligands but bidentate and polydentate ligands as well. They are usually prepared by direct reaction between a vanadium trihalide and the ligand. All operations are performed under vaccuum since the complexes are unstable to air and usually moisture. With unidentate ligands (L), complexes of the type $[VL_6]^{3+}X_3^-$, $[VL_4X_2]^+X^-$, $[VL_3X_3]$, and $[VL_2X_3]$ as well as several anionic types are formed. Bidentate ligands (B) form complexes of the type $[VB_3]X_3$ and $VX_3 \cdot 1{>}B$.

Tridentate ligands (T) form complexes of the type $[VX_3T]$. Reactions of multi-dentate ligands having more than three donor atoms with vanadium (III) need further research.[10]

V(IV)d^1

Under ordinary conditions, the most stable oxidation state for vanadium is (IV). Thus, aqueous solutions of V(III) are oxidized by air to V(IV) and V(V) is readily reduced to V(IV) by mild reducing agents.[7]

Known tetrahalides include VF_4, VCI_4, and VBr_4. The chloride and bromide are believed to exist as tetrahedrally arranged monomeric species. The flouride is thought to exist as a flourine-bridged polymer of VF_6 units each sharing four flourine atoms with adjacent units. The exact structure, however, is not known with certainty.[9]

The oxyhalides of V(IV) have not been investigated in detail but the compounds $VOCI_2$, $VOBr_2$, and VOF_2 have been prepared. The oxyiodide apparently has not been prepared. The oxide of V(IV) is the dark blue VO_2. It is amphoteric, being soluble in both acids and bases.

Some of the more important V(IV) compounds are those that contain the VO unit, which can persist through a variety of chemical reactions. In fact, the VO^{2+} ion is believed to be the most stable diatomic ion known. It forms a wide variety of stable complexes which may be cationic, neutral,

or anionic. Most V(IV) complexes are of the type $[VOL_5]^{n+}_{-}$, $[VOL_4]^{n+}_{-}$, $[VOLxL'_{5-x}]^{n+}_{-}$ or $[VOL_xL'_{4-x}]^{n+}_{-}$. Examples are $R_3[VOF_5]$, $R_2[VOF_4]$, $VOCI_2.3DMSO$, and $VOCI_2.2C_5H_5N$. Electronegative donor atoms such as F, CI, O and N form the strongest bond with oxovanadium (IV).[10]

Much structural work has been done on oxovanadium (IV) compounds. The characteristic feature is one short V=O bond per vanadium. The stereochemistry of the five-coordinate complexes is that of the square pyramid. The six-coordinate complexes are a type of distorted octehedron.[7]

V(V)d^o

In the group oxidation state (V), vanadium is diamagnetic and gives rise to compounds that are usually colorless or pale yellow.[8] It forms halogen compounds with flourine only. The non-existance of other pentahalides is attributed to either steric effects or more probably thermodynamic effects associated with the higher bond energy of the other halides relative to flourine. VF_5 is a white solid which melts to a pale yellow viscous liquid at 19.5°C. The crystal structure has yet to be determined but the volatility of the compound compared to other vanadium flourides suggests a polymer.[10]

Oxytrihalides of all the halogens but iodine have been prepared. They are all hygroscopic and monomeric

with C_3v symmetry in the vapour state. Vanadium dioxyflouride and dioxychloride have also been prepared. The dioxychloride is an orange, hygroscopic, crystalline solid which is probably polymeric. Very little is known about the dioxyflouride.[10]

The oxide of V(V) is V_2O_5. It is the only vanadium oxide of any commercial significance. Vanadium pentoxide is a yellowish-red powder that is slightly soluble in water. It is amphoteric so is much more soluble in acids or bases. It forms an irregular layer structure where each vanadium atom has an environment of five oxygen atoms in a distorted trigonal-bipyramid[8] or possibly a distorted tetragonal pyramidal arrangement.[10]

The dioxovanadium (V) ion, formed under strong acid conditions, is capable of forming complexes with anions other than ClO_4^- or $CF_3SO_3^-$. For example, in HCl, the complex cis-$[VO_2Cl_4]^{3-}$ is formed. Complexes such as cis-$[VO_2EDTA]^{3-}$,[11] cis-$[VO_2Ox_2]^{3-}$,[12] and $K_2[VO_2F_3]$[13] have also been prepared. The cis arrangement for dioxo compounds of metals with no d-electrons (vanadium V) is preferred over the trans arrangement because the strongly π donating O ligands have exclusive share of one d orbital each (dxz, dyz) and share a third one (dxy). If the O ligands were in the trans arrangement, they would have to share two d orbitals and leave one unused.[7]

When V_2O_5 is dissolved in 30% H_2O_2 or when H_2O_2 is added to acidic V(V) solutions, oxygen atoms on the vanadate are replaced by one or more O_2^{2-} groups giving red peroxo complexes. Several peroxo-vanadate complexes have been isolated and structurally characterized. These will be discussed in more detail below.

Only a few non-oxovanadium (V) complexes exist since common ligands often reduce vanadium pentaflouride to the quadrivalent state. Simple adducts of the type VF_5L or $VF_5.2L$ are not known. The best defined complexes of vanadium (V) are the hexaflourovanadates $M'VF_6$ (M=K or Ag) and $Ba(VF_6)_2$.[7]

2.2 AQUEOUS CHEMISTRY OF VANDIUM

In aqueous solution, vanadium in the (II) and (III) states exists mainly as $[V(H_2O)_6]^{2+}$ and $[V(H_2O)_6]^{3+}$ ions respectively. Both ions are oxidized by air and $[V(H_2O)_6]^{2+}$ is oxidized by water with the evolution of hydrogen. The ions may be generated by dissolving the appropriate vanadium halide or by electrolytic or chemical reduction of acidic solutions of V (V), V (IV), or V (III).

The aqueous chemistry of V (IV) involves mainly the $[VO(H_2O)_5]^{2+}$ ion. As mentioned before, a wide range of compounds can be obtained from these solutions.

The aqueous chemistry of V (V) has been studied intensively by a wide variety of physical methods to determine the nature of the various species present. However, there are still serious differences in the formulations given to some of these species.

Vanadium pentoxide dissolves in NaOH to give colorless solutions. There is little doubt that $[VO_4]^{3-}$ (aq.) is the predominate species present at this high pH. (The (aq.) represents an unknown degree of hydration.) The $[VO_4]^{3-}$ (aq.) ion is a moderately strong base and is hydrolyzed

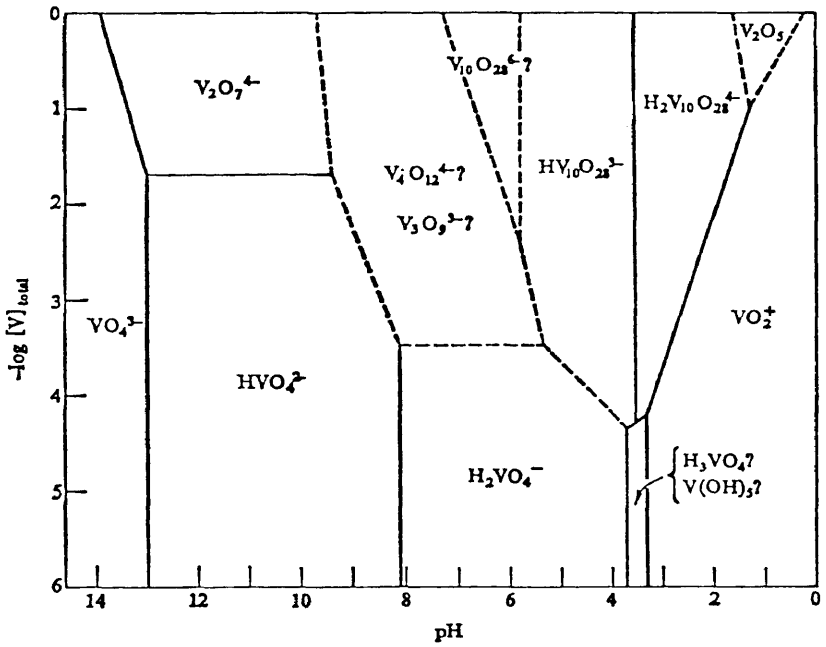
in solutions of pH range 8 to 13 to form the $[HVO_4]^{2-}$ (aq.) ion. This species can condense to form the $V_2O_7^{4-}$ (aq.) ion or can be protonated in the pH range 4 to 8 to form the $[H_2VO_4]^-$ (aq.) ion.[9]

The nature of the species formed by the polymerization of the $[H_2VO_4]^-$ (aq.) ion is still in question. The problems arise from the inability to prove conclusively which polymeric species exists in the pH range 6.5 to 8.2. Much of the information gathered suggests it to be the trimer $[V_3O_9]^{3-}$ (aq.). However a considerable amount of evidence supports the view that the tetramer $[V_4O_{12}]^{4-}$ (aq.) is the predominant species. Some believe the trimer and tetramer are in equilibrium with one another,[14] while others[8] believe the trimer exists at lower vanadium concentrations and the tetramer at higher concentrations.

Simple protonation of the $[H_2VO_4]^-$ (aq.) ion yields uncharge vanadic acid. This species polymerizes very easily to form various decanuclear ions that have been represented as $[H_2V_{10}O_{28}]^{4-}$ (aq.), $[HV_{10}O_{28}]^{5-}$ (aq.), and possibly $[V_{10}O_{28}]^{6-}$ (aq.).[8] Further protonation of the $[H_2V_{10}O_{28}[^{4-}$ (aq.) ion, at a pH below 3.2, results in its depolymerization to the $[VO_2](aq.)^+$ ion. Recent studies have indicated that in concentrated $HClO_4$ and H_2SO_4, the $[VO_2]$ (aq.)+ ion dimerizes to the $V_2O_3^{4+}$ ion.[15]The ranges of existence

of the various species at different vanadium concentrations and pH are summarized in figure 2.2.1.[9]

Figure 2.2.1



The approximate conditions of pH and total vanadium concentration under which a given species would be the major solute component of a vanadate solution at 25°C. Demarcation lines about which there is doubt are dashed.

2.3 PEROXO COMPLEXES OF VANADIUM (V)

Vanadium (V) has the d^0 electronic configuration and therefore is capable of forming complexes with a host of electron rich ligands, including the peroxo group. The simplest peroxovanadium complexes are the peroxovanadates formed upon addition of H_2O_2 to mildly acidic or basic solutions of V_2O_5. These compounds are moderately well characterized and may contain 4,3,2, or 1 peroxo groups per vanadium atom. For example, reacting concentrated solutions of V_2O_5 with H_2O_2 in concentrated alkali hydroxide at temperatures below 0^oC give blue solutions containing the $V(O_2)_4^{3-}$ ion whereas the product of this reaction in mildly acidic media is the monoperoxy-oxovanadate cation $V(O)(O_2)^+$.[16] It has been concluded that in aqueous solution (a) the number of peroxo groups per vanadium atom increases with the alkalinity, (b) increasing the acidity increases the polymerization and decreases the number of peroxo groups per vanadium atom and (c) increasing the concentration of H_2O_2 decreases the degree of polymerization.[10]

The structural data on the complexes investigated generally supports the bidentate model of the peroxo group coordination, although coordination can range from an ideally

symmetrical bidentate to a terminal monodentate position capable of forming bridging V(V) peroxo derivatives. Structural studies have revealed a fairly constant 0-0 bond length ranging from 1.42 to 1.47$\mathring{A}$. This does not differ significantly from the oxygen distances found in the peroxo ion or hydrogen peroxide itself. Therefore the peroxo group is regarded as a bidentate ligand.[17]

The peroxo group is bound to the metal via the expected σ and $p\pi$ type bonding and since V(V) has the d^0 electron configuration, additional $p\pi^*$ electron delocalization is anticipated.

Heteroligand peroxo complexes possess mixed ligand spheres composed of one to three coordinated peroxo groups, and one or more monodentate or polydentate ligands. Heteroligands range from monodentate halide ions to bulky organic molecules.

Since vanadium has a strong tendency to form oxoperoxo species, the stereochemistry of most heteroligand peroxo complexes of vanadium (V) is that of the pentagonal bipyramid with the oxo group in the axial position and the peroxo groups in the cis position.[18] For example $NH_4[VO(O_2)_2(NH_3)]$[19] was determined to have pentagonal pyramidal symmetry with the four oxygens of the two peroxo groups and the ammonia nitrogen atom forming the base of the pyramid and the vanadyl oxygen occupying the apical position. K_3[VO

$(O_2)_2(C_2O_4)]\cdot H_2O$[20] is pentagonal bipyramidal in shape with the vanadyl oxygen and an oxygen from the oxalate group at apices, while the four oxygens from the peroxo groups and an oxygen from the oxalate forming a type of pentagonal plane. The water molecule is weakly involved in hydrogen bonds to the oxalate and peroxo groups. $NH_4[VO(O_2)(H_2O)(C_5H_3N(COO)_2)]\cdot XH_2O$ ($X \approx 1.3$)[21] is pentagonal bipyramidal in shape with the vanadyl oxygen and a water molecule at the apices and the peroxo group, the nitrogen from the pyridine ring, and one oxygen from each carboxylate group forming an approximate pentagonal plane. $VO(O_2)$ (Picolinic Acid) $2H_2O$[22,23] complexes have a distorted pentagonal bipyramid shape with the apical positions being occupied by the vanadyl oxygen and a water molecule, while the oxygen atoms of the peroxo group, an oxygen and a nitrogen atom from the picolinate ligand and a water molecule form the pentagon.

2.4 ELECTROCHEMISTRY OF VANADIUM

The electrochemistry of vanadium is characterized by the following thermodynamic potentials:[24]

$V^{2+} + 2e^- \rightleftharpoons V$		$E^o=-1.2$ V
$V^{3+} + e^- \rightleftharpoons V^{2+}$		$E^o=-0.255$V
$V^{5+} + e^- \rightleftharpoons V^{4+}$(1fNaOH)		$E^o=-0.74$V
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$		$E^o=0.337$V
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$		E=1.00V
$V(OH)_4^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$		$E^o=1.00$V
$V(OH)_4^+ + 4H^+ + 5e^- \rightleftharpoons V + 4H_2O$		$E^o=0.25$V

From this information, one can see that acidic solutions of vanadium (V) are moderately good oxidizing agents, and that solutions of oxovanadium (IV) are stable when acidic but are oxidized by air when alkaline.

In the presence of complexing agents, thermodynamic potentials are shifted from moderate to large degrees depending upon the type of ligand and the pH.

2.5 ELECTROCHEMISTRY OF THE PEROXO GROUP

In aqueous solutions, the redox chemistry of H_2O_2 is summarized by the following potentials:

$$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O \qquad E^o = 1.77V$$

$$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2 \qquad E^o = 0.68V$$

$$HO_2^- + H_2O + 2e^- \rightleftharpoons 3OH^- \qquad E^o = 0.87V$$

One can see from this information that H_2O_2 is a strong oxidizing agent in both acidic and basic solutions. Only with very strong oxidizing agents such as MnO_4^- or Ce^{4+} will it behave as a reducing agent.[7]

While the reduction of hydrogen peroxide is a two-electron process in aqueous solutions, studies[25] in aprotic solvents indicate that the reduction proceeds via a one-electron process followed by a chemical reaction between the product species and another solvated peroxide molecule forming the superoxide ion.

$$H_2O_2 + e^- \rightleftharpoons HO_2^- + 1/2H_2$$

$$HO_2^- + H_2O_2(sol) \rightleftharpoons O_2^- + H_2O$$

Insight into the oxidation of peroxide may be gained through mechanistic studies[26,27,28] the reduction of O_2

in aqueous and aprotic solutions. Experimental observations clearly support the conclusion that the first step in the reduction of O_2 in both aqueous and aprotic solutions is a one-electron reduction to superoxide ion

$$O_2 + e^- \rightleftharpoons O_2^-$$

followed by either a second irreversible reduction if the solvent is aprotic (with the solvent involved)

$$O_2^- + e^- \rightleftharpoons HO_2^- \qquad E^o = -2.0V$$

or by chemical disproportionation reactions to yield H_2O_2 under acid conditions or OH^- under basic conditions.[27] Long lifetimes are observed for the superoxide ion in aprotic as well as strongly alkaline solutions, but not in non-alkaline solutions.

The effect of protons on the electrochemical reduction of oxygen in aprotic media is dramatic. As the concentration of protons is increased, the reduction potential becomes more positive and the one-electron process gives way to an apparent irreversible two-electron process.[26]

2.6 POTENTIOMETRIC TITRATIONS

Since the potential of galvanic cells depend upon the activities of certain ionic species in the cell solution, the endpoint of a titration may be detected by determining the volume of titrant at which a relatively large change in potential occurs as the titrant is added. The potentiometric method can be employed for all the reactions used for titrimetric purposes: acid-base, redox, precipitation, and complex formation.[29] The cell simply consists of a proper indicator electrode and a reference electrode. The titration may be performed manually or may be automated.

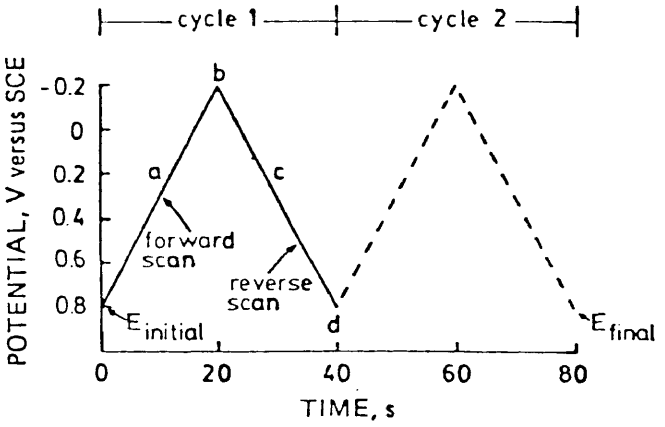
In our work, we have utilized potentiometric titrations to study the oxidation of the peroxo group in acid solutions of various vanadium (V) complexes using cerium (IV), $KMnO_4$, and $K_2Cr_2O_7$ as oxidants. Standard potentials of these strong oxidants are +1.61V,+1.51V, and +1.33V respectively.[29] They all are therefore able to oxidize peroxides in acid solutions.

2.7 PRINCIPLES OF CYCLIC VOLTAMMETRY

Cyclic voltammetry is a valuable electroanalytical technique for the study of electroactive species. Its versatility combined with ease of measurement has lead to its extensive use in the field of electrochemistry, inorganic, organic, and biochemistry.

The experiment consists of cycling the potential of an electrode immersed in an unstirred solution and measuring the resulting current. The potential of this "working electrode" is controlled versus a reference electrode. The controlling potential which is applied across these two electrodes can be considered an "excitation signal". The excitation signal for C.V. is a linear potential scan with a triangular waveform as shown in fig. 2.7.1[30]

Figure 2.7.1

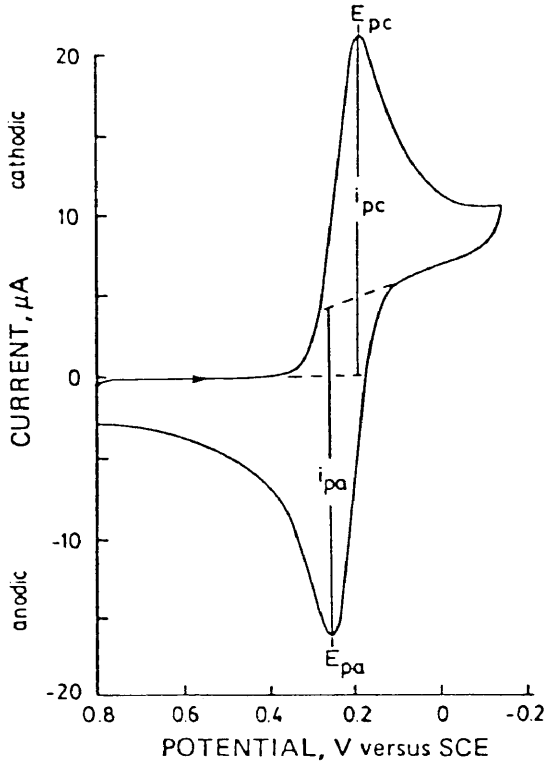


Typical excitation signal for cyclic voltammetry—a triangular potential waveform with switching potentials at 0.8 and −0.2 V versus SCE.

The triangular potential excitation signal sweeps the potential of the electrode between "switching potentials" (+0.8V and -0.2V in fig. 2.7.1). A cyclic voltammogram is obtained by measuring the current at the working electrode during the potential scan. The current can be considered the "response signal" to the potential excitation signal. A voltammogram is a plot of the current (vertical axis) versus potential (horizontal axis). In a sense, a voltammogram is analogous to a conventional spectrum in that it conveys information as a function of an energy scan.[30]

Figure 2.7.2[30] shows a current-voltage plot (voltammogram) for $Fe(CN)_6^{3-}$

Figure 2.7.2



The initial potential E_I at +0.8V is chosen to avoid any electrolysis of $Fe(CN)_6^{3-}$ when the electrode is turned on. As the potential is scanned in the negative direction, the current rises to a peak and then decays in a regular manner. The current depends on two steps in the overall process; the movement of electroactive material to the electrode surface and the electron transfer reaction. The electron transfer rate constant for a reduction process is a function of the potential and can be described theoretically.

$$K_f = K^o \exp\left[\frac{-\alpha nF}{RT}(E - E^{ol})\right]$$

K^o is the standard heterogeneous electron-transfer rate constant whose value is a property of the reaction between the particular compound and the electrode surface used, n is the number of electrons transferred per molecule, F is Faraday's constant, R is the universal gas constant, and T is Kelvin temperature. E^{ol} is the formal reduction potential combined with activity coefficients for a term that is subject to solution conditions, and α is the transfer coefficient factor arising because only a fraction of the energy put into the system (applied potential) lowers the activation energy barrier.[31]

The exponential dependence of K_f on the applied potential accounts for the steep rise in the current. However, electrolysis of the reactant depletes its concentration near the electrode surface. Since the experiment is performed at a stationary electrode in an unstirred solution, diffusion is the principal means of moving the reactant to the surface. As the concentration gradient continues to decrease, the rate of mass transport continues to decrease causing the current to decay. Finally, the current becomes controlled by the rate of diffusion and independent of the applied potential.[31]

The advantage of cyclic voltammetry is that a significant concentration of the product (in our example the reduced form) has been generated near the electrode surface on

the forward scan. When the scan direction is reversed, the reduced form is oxidized back to the original starting material and the current for this reverse process is recorded. The current is a function of the applied potential and the rate of diffusion as above.[31,32]

One of the many uses of C.V. is in the determination of formal reduction potentials of systems where the electron transfer process is reversible and the diffusion coefficients for the oxidized and reduced forms are similar. To be electrochemically reversible, the reaction

$$O + e^- \underset{K_b}{\overset{K_f}{\rightleftharpoons}} R^-$$

must be fast enough to maintain the proper equilibrium concentrations of oxidized and reduced forms as is dictated by the Nernst equation:[31]

$$E = E^o - \frac{RT}{nF} \ln \frac{[R]}{[O]}_{x=0}$$

If the system is reversible, the separation in the peak potentials, E_p will be close to $\frac{58}{n}$mV. at 25°C and will be independent of the scan rate. However, many systems appear to be reversible when the voltage is scanned slowly but at higher scan rates E_p becomes greater than $\frac{58}{n}$mV. This is because the rate constants K_f and K_b of the heterogeneous electron transfer reaction are finite, so a scan

rate exists for all systems that is high enough that the electrode reaction will no longer be able to maintain equilibrium conditions as the potential changes.[30] Reversibility then, is a matter of degree and depends on the stress applied to the system.

Systems where $E_p > \frac{58}{n}$ mV are irreversible. This occurs when $K_f >> K_b$ for the cathodic peak and $K_b >> K_f$ for the anodic peak. Such situations commonly occur when reactions yield products that cannot be recycled electrochemically to give back the original reactants. One of the most useful aspects of cyclic voltammetry is its application to the qualitative diagnosis of these homogeneous chemical reactions that are coupled to the electrode surface reaction. C.V. provides the capability for generating a species during a forward scan then exploring its fate on the reverse scan and subsequent cycles.[30]

One can easily identify cases where the product of the electrode reaction is lost via chemical reaction because the return peak will be reduced in magnitude. If the reaction half-life is less than the scan duration, the return peak may be completely absent.[33]

Such a reaction scheme is designated EC, where E signifies the electrochemical step and C the following chemical reaction. The C step can be first or second order, irreversible or reversible. More complex reaction schemes are denoted

by a string of letters in the order of the steps in the reaction scheme such as CE, ECE, ECEC, EEC etc. Subscripts are often added to denote reversibility, reaction order or other special cases.[33] Table 2.7.1[31] provides examples of a number of possible reaction mechanisms and their letter designations.

Table 2.7.1

Electrochemical Mechanisms Involving Coupled Chemical Reactions

I. Reversible electron transfer, no chemical complications

$$O + ne \rightleftharpoons R$$

II. Reversible electron transfer followed by a reversible chemical reaction—E_rC_r mechanism

$$O + ne \rightleftharpoons R$$

$$R \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Z$$

III. Reversible electron transfer followed by an irreversible chemical reaction—E_rC_i mechanism

$$O + ne \rightleftharpoons R$$

$$R \overset{k}{\rightarrow} Z$$

IV. Reversible chemical reaction preceding a reversible electron transfer—C_rE_r mechanism

$$Z \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O$$

$$O + ne \rightleftharpoons R$$

V. Reversible chemical reaction preceding an irreversible electron transfer—C_rE_i mechanism

$$Z \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O$$

$$O + ne \rightarrow R$$

VI. Reversible electron transfer followed by an irreversible regeneration of starting material—catalytic mechanism

$$O + ne \rightleftharpoons R$$

$$R + Z \overset{k}{\rightarrow} O$$

VII. Irreversible electron transfer followed by an irreversible regeneration of starting material

$$O + ne \rightarrow R$$

$$R + Z \overset{k}{\rightarrow} O$$

VIII. Multiple electron transfer with intervening chemical reaction—ECE mechanism

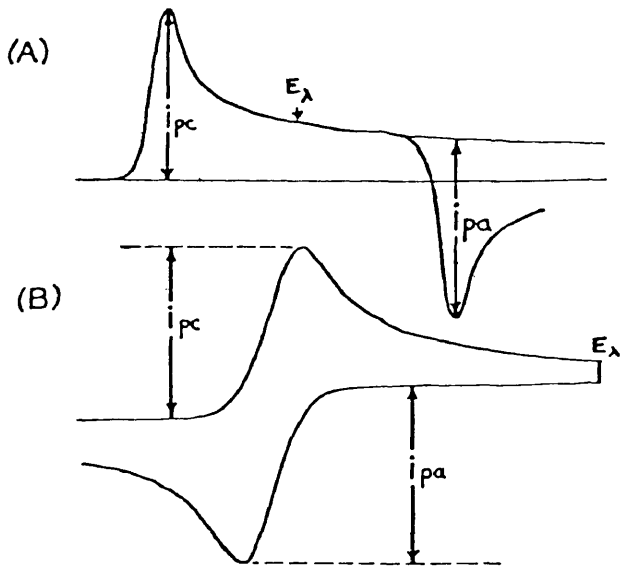
$$O + n_1e \rightleftharpoons R \quad R \rightleftharpoons Y$$

$$Y + n_2e \rightleftharpoons Z$$

Perhaps the biggest liability of cyclic voltammetry is the difficulty associated with establishing the correct baseline for measuring the magnitudes of the peak currents $i_{P(a)}$ and $i_{P(C)}$. Measurement of the baseline for the forward scan is simply a matter of recording a scan containing only the supporting electrolyte solution under identical

scan conditions as the analyte solution. The reverse scan is more complicated since the electrolysis of the forward process contributes to the total current until the scan has passed the foot of the forward wave again. One generally accepted approach is to assume the contribution of the forward process to the total current continues to decrease with the square root of the time during the reverse scan. The baseline curve for the return scan can be obtained by stopping the forward scan at the switching potential E while the recorder continues to sweep along the x-axis recording current as a function of time. This is shown in figure 2.7.3A.[31] Another approach is to stop and hold the scan at the switching potential until the current becomes fairly constant, then proceed. This is shown in fig. 2.7.3B.[31]

Figure 2.7.3 A&B



In summary, cyclic voltammetry provides a simple yet effective means for studying redox states. It allows a wide potential range to be scanned for reducible or oxidizable species. This quality along with its variable time scale and good sensitivity make C.V. one of the most versatile electroanalytical techniques yet developed. However, it must be realized that while C.V. is a powerful qualitative technique, the limitations to its use in quantitative measurements are considerable.[30] The real forte of C.V. is in its application to the qualitative diagnosis of electrode reactions which are coupled to homogeneous chemical reactions.

3. EXPERIMENTAL

3.1 POTENTIOMETRIC OXIDATION OF PEROXOVANADIUM (V) COMPLEXES

The potentiometric titrations were performed on a Metrohm 655 Dosimat connected to a Brinkmann Potentiograph E 536. The potential changes were measured with a saturated calomel-platinum wire combination electrode.

Procedure to run titrations

15 to 25 mg. of the sample was dissolved in 8 ml of 1M H_2SO_4. This solution was then diluted with 8 ml of deionized water to give a final solution that was 0.5M in acid. The appropriate oxidant was added at a rate of 10 ml per 20 minutes. From this tracing, the amount of sample necessary to cause the final inflection to occur near 7.5ml was determined. This amount of sample was then weighed, treated as above then titrated at a rate of 10 ml per 200 minutes.

3.1.1 Ce (IV) AS AN OXIDANT

Cerium in the quadrivalent state (4+) is a powerful oxidizing agent undergoing the reaction,

$$Ce^{4+} + e^- \leftrightarrows Ce^{3+}$$

In the presence of peroxide ion the reaction

$$2Ce^{4+} + H_2O_2 \rightarrow 2Ce^{3+} + O_2 + 2H^+$$

takes place.

However, the reagent cannot be used in neutral or basic solutions since hydrolysis leads to precipitation in solutions of low hydrogen ion concentration. The acidity of solutions containing Ce(IV) must be at least 0.1N or greater to avoid this precipitation.

The redox potential of the Ce (IV/III) couple is dependent on the nature and concentration of the acid present. The formal potential of a 1M H_2SO_4 solution is +1.44V. Sulfuric acid solutions of Ce (IV) ion are extremely stable and can be kept indefinitely without a change in concentration.[29]

Preparation of Cerium (IV) solution

A solution of $(NH_4)_4[Ce(SO_4)_4]\cdot 2H_2O$ was previously prepared by Sandy Craig before my arrival. It was standardized against $K_4[Fe(CN)_6]$ and found to be 0.05064N.

3.1.2 PERMANGANATE ION AS AN OXIDANT

Permanganate undergoes a number of reactions since manganese can exist in the oxidation states +2,+3,+4,+6

and +7. However, potassium permanganate is most commonly employed with solutions that are 0.1N or greater in acidity under which conditions the reaction,

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O \quad E^o = 1.51V$$

occurs. In the presence of peroxide, the reaction,

$$2MnO_4^- + 5H_2O_2 + 6H^+ \rightleftharpoons 2Mn^{2+} + 5O_2 + 8H_2O$$

takes place.

Potassium permanganate is a strong oxidant and its intense purple color often can act as its own indicator. These qualities along with its moderate price allow it to perhaps be the most widely used of all standard oxidizing agents. However there are limitations. The multiplicity of possible reaction products can, at times, cause uncertainty regarding the stoichiometry of a permanganate oxidation, plus light or traces of MnO_2 can lead to decomposition. Yet, when proper precautions are taken, the concentration of a standardized permanganate solution will not change appreciably over a period of several months.[29]

Preparation of $KMnO_4$ solution

4.87g.$KMnO_4$ was dissolved in 3 liters of deionized water and boiled gently for 20 minutes. After cooling the solution was filtered through a sintered glass funnel and poured into a dark glass bottle and stored in a dark

cabinet. The solution was standardized with standard $K_4Fe(CN)_6$. The concentration was determined to be 0.05318N.

3.1.3 DICHROMATE AS AN OXIDANT

Potassium dichromate is not as strong an oxidant as Ce(IV) or MnO_4^-. It is, however, inexpensive, very stable in solution, and can be obtained sufficiently pure to prepare standard solutions by weighing.[29] In the presence of peroxide, the following reaction occurs:

$$Cr_2O_7^{2-}+8H^+ +3H_2O_2 \rightleftharpoons 2Cr^{3+}+3O_2+7H_2O$$

Preparation of $K_2Cr_2O_7$ solution

2.46083 g. A.C.S. grade $K_2Cr_2O_7$ was dissolved in 1 liter of deionized water for a final concentration of 0.050185N.

3. EXPERIMENTAL

3.2 CYCLIC VOLTAMMETRY

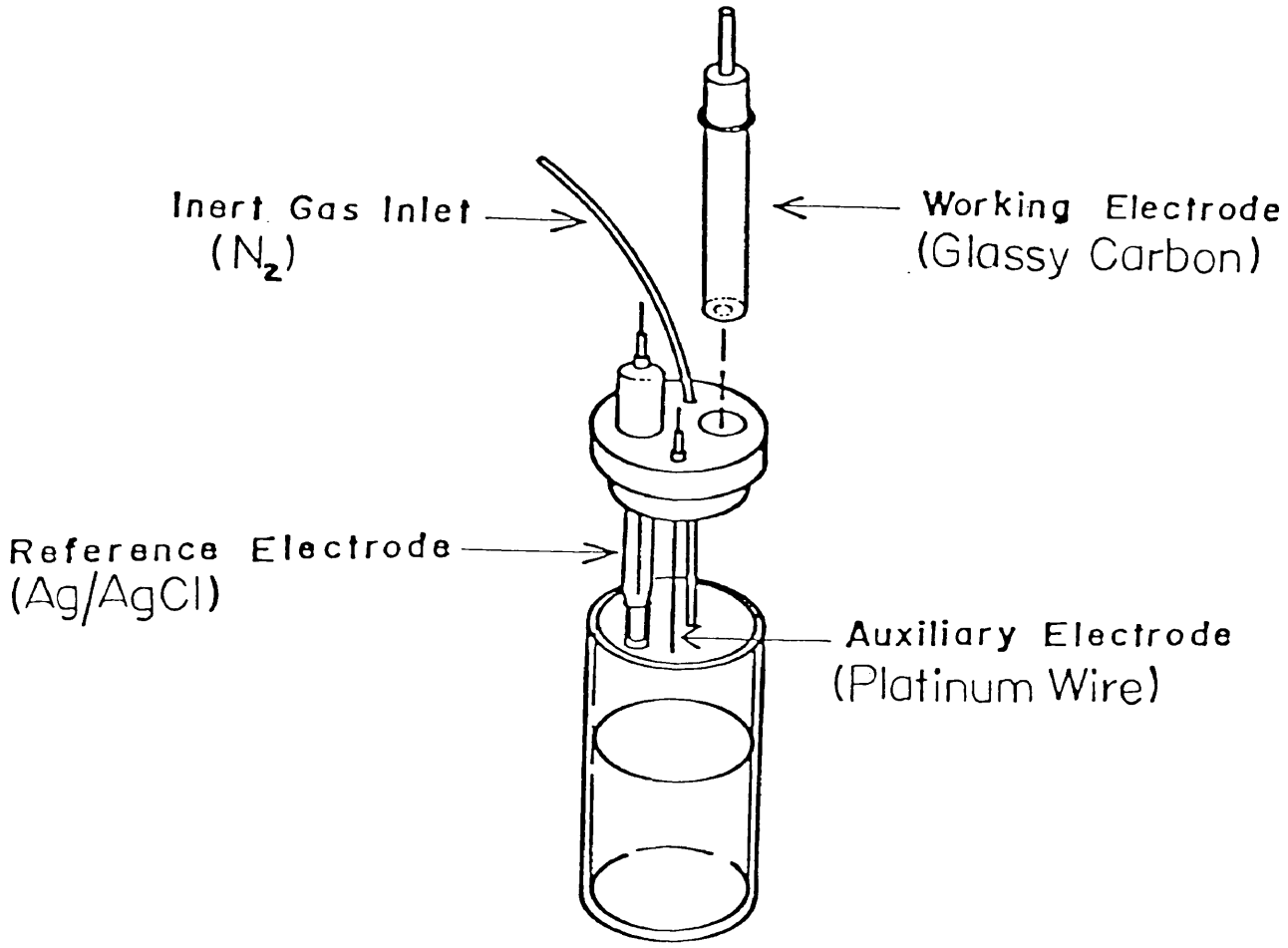
Cyclic voltammetry experiments were performed on a BAS model CV-1B cyclic voltammetry instrument connected to a Houston Instrument Omnigraphic 100 recorder. The electrolytic cell was composed of a glassy carbon working electrode, a 3M(NaCl) Ag/AgCl reference electrode, and a platinum wire auxiliary electrode (see fig. 3.2.1). The pH of the $LiClO_4$ solutions was measured with an Orion Research model 231 portable pH/mV/temperature meter. The pH meter was calibrated using commercial buffers of pH=4.01 and 7.00.

3.2.1. Procedure to Run Voltammograms

The electrolyte/analyte solutions can be divided into two groups: simple solutions of a peroxovanadium complex dissolved in the appropriate electrolyte, and solutions comprised of all the components in the complex made by mixing the individual solutions of the components.

The solutions of the complexes are prepared by dissolving 30 to 35 mg. of the analyte compound in 15 ml of the appropriate 0.2M electrolyte to obtain approximately 10^{-3}M V(V)

Figure 3.2.1


Inert Gas Inlet
(N_2)
Working Electrode
(Glassy Carbon)
Reference Electrode
(Ag/AgCl)
Auxiliary Electrode
(Platinum Wire)

solutions. The solutions composed of component solutions were made by pipetting 20 ml of a 2.5×10^{-3}M V(V) solution, 10 ml of a 5.4×10^{-3}M H_2O_2 solution, 10 ml of a 0.01M heteroligand solution, and 10 ml of the 1M electrolyte solution into a beaker and mixing. Final solutions therefore contain 1×10^{-3} V(V), 1×10^{-3}M H_2O_2, 2×10^{-3}M heteroligand, and 0.2M background electrolyte.

The electrolyte/analyte solution was poured into the cell. N_2 gas was bubbled through the solution for approximately 5 minutes to remove dissolved O_2. The solution was then allowed to stand for about 1 minute to become still.

Before each voltammogram, the working electrode was resurfaced by polishing. This involved gently rubbing the face of the electrode in a circular motion for approximately 10 to 15 seconds on a moist polishing pad with a few drops of alumina polishing compound. The alumina abrasive was washed away with a stream of deionized water.

All voltammograms were initiated at a potential between 600 and 400 mV since this generally avoided the electrolysis of analyte material when the electrode was switched on. All voltammograms, except where indicated, were initiated with a cathodic scan. The switching potentials were not pre-determined. The scan direction was switched manually at the potentials at which water was reduced (cathodic scan) or oxidized (anodic scan).

Generally 3 cycles were run, each being denoted on the voltammogram by a different color. During a cycle the scan was stopped at the appropriate potential (usually the starting potential) and the pen color was changed. The process took only a few seconds and the scan was resumed. The color sequence was always red for the first cycle, black for the second cycle, and green for the third. If a fourth cycle was run or a blank electrolyte solution was run, the scan color was blue.

All variable parameters with the exception of current sensitivity were kept constant for ease of comparison. The scan rate was fixed at 100 mV/sec., the potential sensitivity was fixed at 200mV/cm, the filter was fixed at 0.001 seconds, and all voltammograms were run at room temperature.

3.2.2 Lithium Perchlorate Solutions

160 g. $LiClO_4 \cdot 3H_2O$ was dissolved in deionized water in a 1000 ml volumetric flask. The water became cold upon dissolution. The solution was allowed to warm to room temperature then brought up to volume to get a 1M solution.

3.2.3 Perchloric Acid Solutions

666.7 g. of 60% $HClO_4$ was diluted to 4000ml to obtain a final concentration of 1M $HClO_4$.

3.2.4 Sulfuric Acid Solutions

50.5 g. of concentrated sulfuric acid was diluted to 500 ml to obtain a final concentration of 1M H_2SO_4.

4. RESULTS AND DISCUSSION

All the solutions studied show strongly irreversible electrochemical processes on the cyclic voltammograms which do not allow quantitative calculations regarding Ep(c), Ep(a), ip(c) and ip(a). Qualitatively, however, the voltammograms are very informative. Qualitative information for all of the systems, except tartrato, is also provided by the potentiometric titrations.

Comparisons have been made between the electroactive species for all of the systems in the following manner:

I) Comparison of electroactive species in non-complexed vanadium (V) solutions with species in the solutions containing complexed vanadates (V).

II) Comparison of the electroactive species in the solutions obtained by dissolving the peroxo heteroligand vanadates in the appropriate electrolyte and recording the cyclic voltammograms immediately with the solutions obtained by mixing stoichiometric amounts of components which include vanadium (V), H_2O_2 and the heteroligands.

III) Comparison of the electroactive species observed in different electrolytes present in excess. In our systems

we have used solutions of 0.2M$LiClO_4$, 0.2MH_2SO_4 and sometimes 0.2M $HClO_4$. Blank electrotyle solutions were run periodically to check the purity of the solutions and the condition of the electrodes.

The potentials of basic interest are E_c(V(V)/V(IV)), and $E_a(O_2^{2-}/O_2)$. Both were observed to be irreversible and therefore peak potentials are discussed here instead of half-wave potentials which are relevant in reversible systems.

E_c(V(V)/V(IV)) and possibly (V(IV)/V(III)) have been found to occur in the range of 250 to -1700mV and depend upon the pH and the ligand. They are almost always clearly resolved.

$E_a(O_2^{2-}/O_2)$ has been observed as a shoulder, sometimes poorly resolved, in the 1400 to 1600mV range.

4.1 PEROXOVANADATES (V) IN THE ABSENCE OF HETEROLIGANDS

To study the electrochemical behavior of peroxovanadates (V) in the absence of heteroligands, voltammograms 4.1.1 through 4.1.7 were taken. Three cycles are shown (curves 1, 2 and 3). The initial starting potential was near 600mV and initial scans were cathodic.

From the cyclic voltammograms of the various systems and the plots of the peak potentials, the following observations are made:

1) On comparing the voltammograms of V(V) (fig. 4.1.3) and V(V)+H_2O_2 (fig. 4.1.4) in 0.2M$LiClO_4$, one sees a considerable difference in the number of peaks present and their potentials. The most obvious differences being the loss of a cathodic peak at -1330mV and the addition of two anodic peaks at 960 and 1160mV when H_2O_2 is present.

2) On comparing the cathodic vanadium (V/IV) peaks near 200 and 50mV one sees a shift toward more positive potentials when peroxide is present.

These results indicate that the peroxo group has a

significant effect on the electro-active species present under these conditions and time frame.

3) On comparing the voltammograms of V(V) in 0.2M$LiClO_4$ (fig. 4.1.3) with the V(V) in 0.2M H_2SO_4 (fig. 4.1.7) one sees a very large difference in the number of peaks and their potentials between the two. This is exactly what one expects considering the dramatic effect pH has on the nature of the vanadium (V) species present in aqueous solution (section 2.2).

4) The effect of H_2O_2 on V(V) in 0.2MH_2SO_4 is seen in figure 4.1.8. The appearance of the cathodic peak at -900 (first cycle) indicates that the peroxo group affects V(V) species present at this low pH.

pH = 3.66

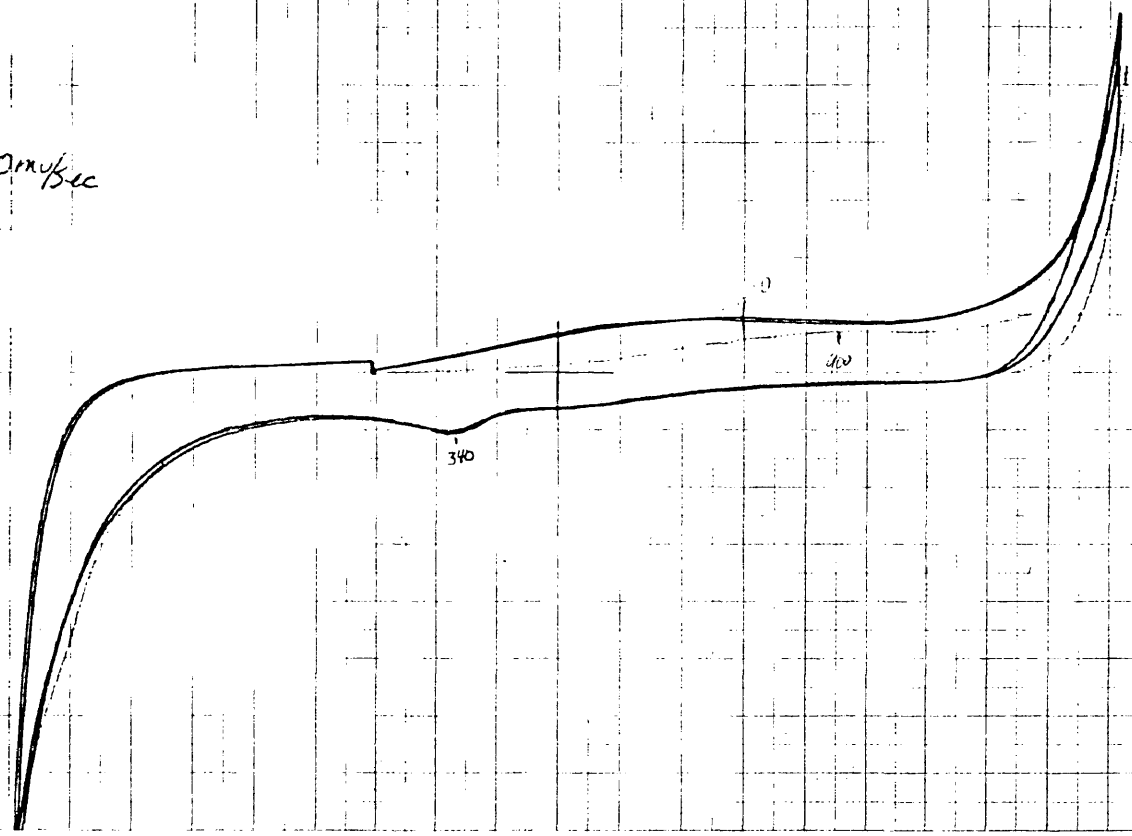
0.2M $LiClO_4$

Fig. 4.1.1

x = 200mV/cm

y = 10uA/cm

Scan rate = 100mV/sec



pH = 4.98

1.08×10^{-3}M H_2O_2

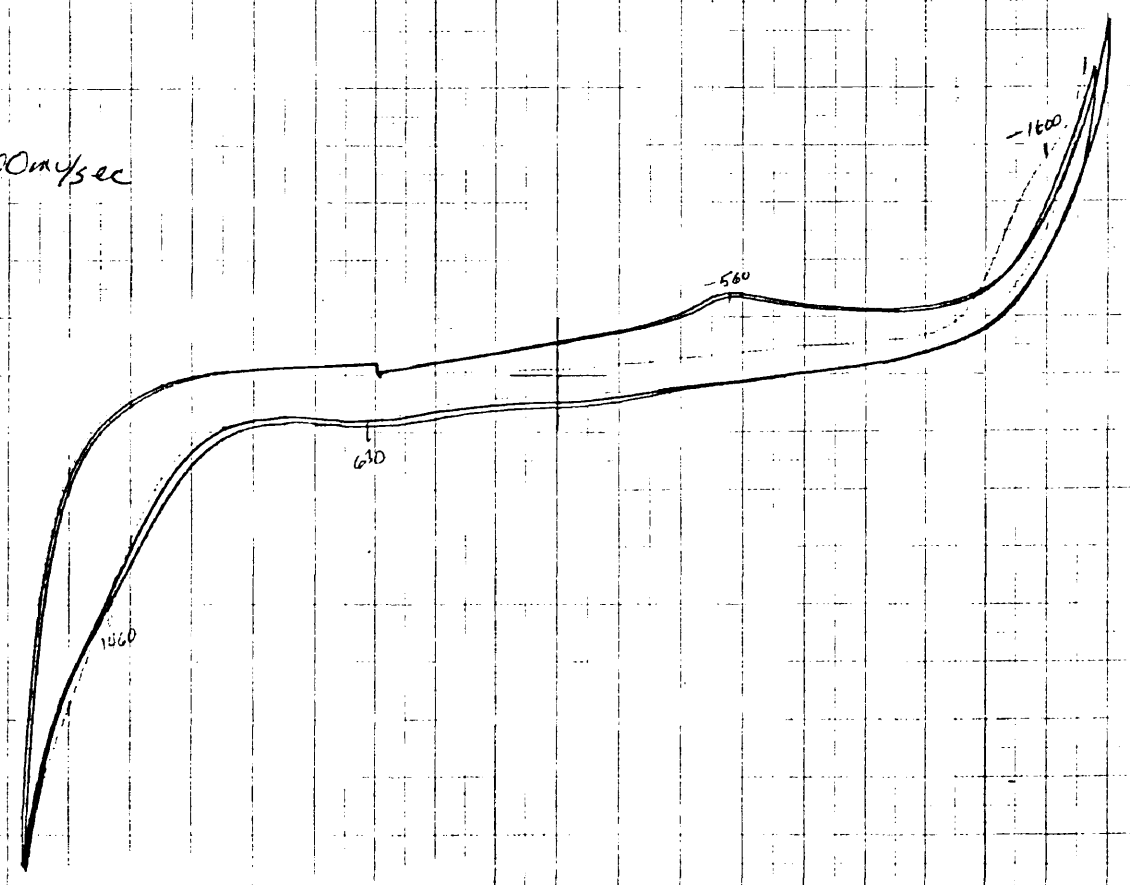
0.2M $LiClO_4$

Fig. 4.1.2

x = 200mV/cm

y = 10uA/cm

Scan rate = 100mV/sec



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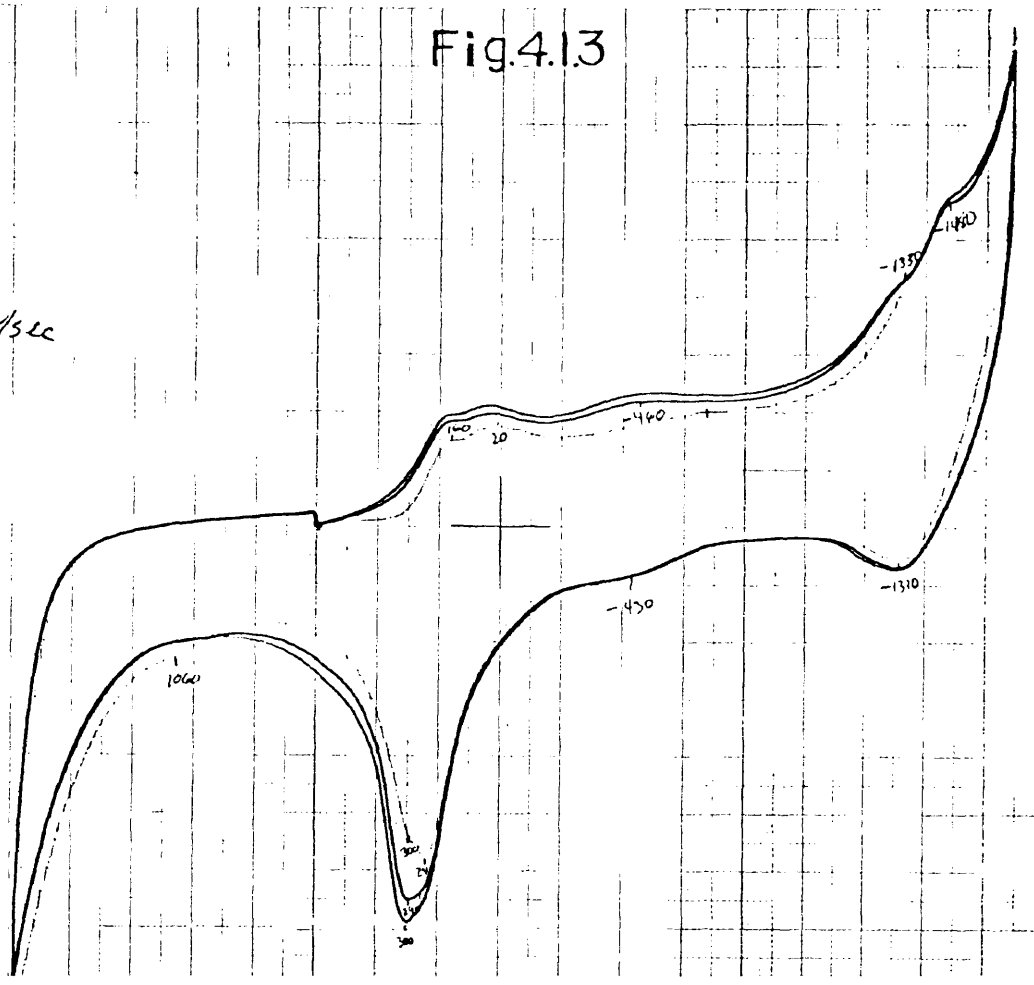
pH 3.10
1.0×10^{-3}M V(V)
0.2M $LiClO_4$

X = 200mV/cm

Y = 5uA/cm

Scan rate = 100mV/sec

Fig.4.1.3



pH = 3.34

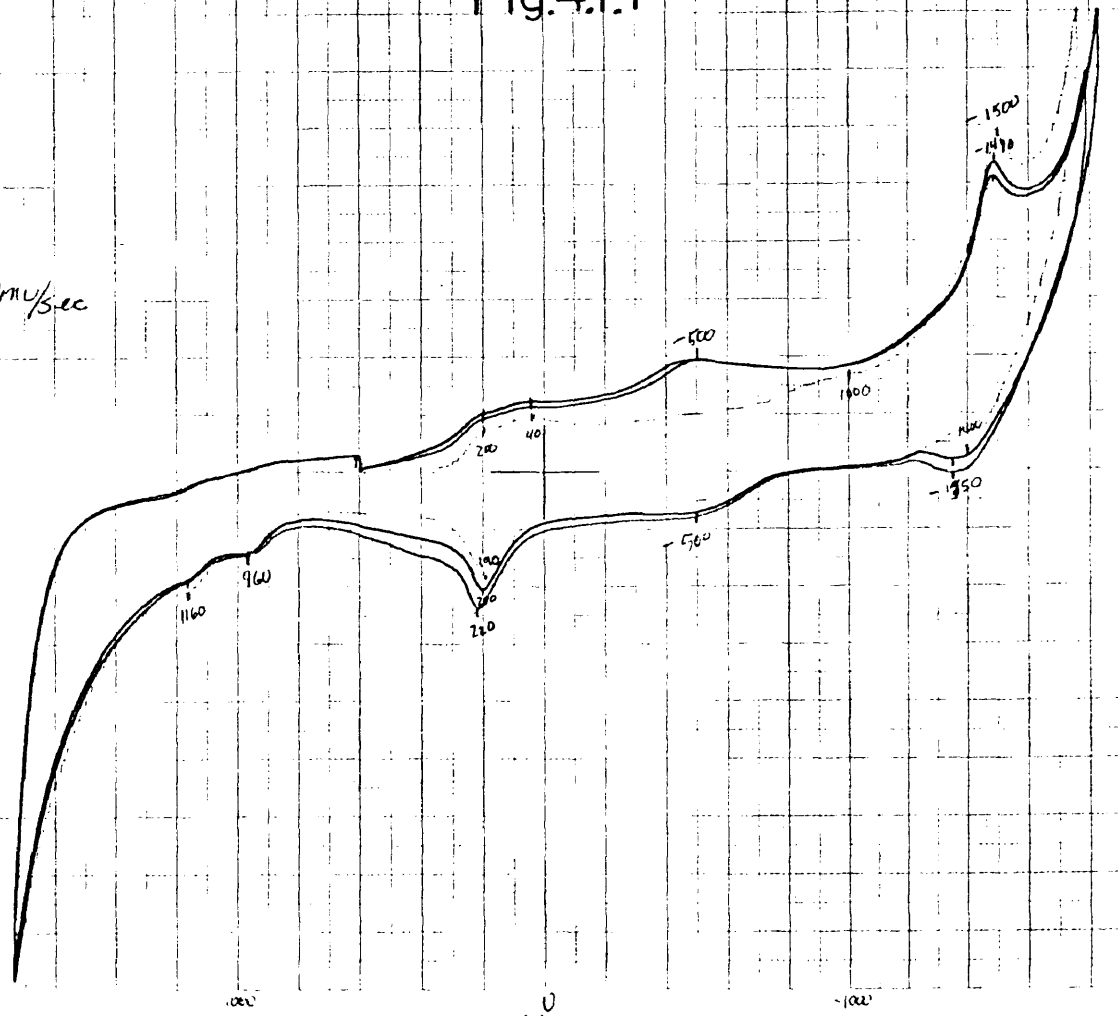
1.0×10^{-3}M V(V)
1.08×10^{-3}M H_2O_2
0.2M $LiClO_4$

X = 200mV/cm

Y = 10uA/cm

Scan rate = 100mV/sec

Fig.4.1.4



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- Fresh sample

Fig.4.1.5

0.2M H_2SO_4

X = 200 mv/cm

Y = 10 μA/cm

Scan rate = 100 mv/sec

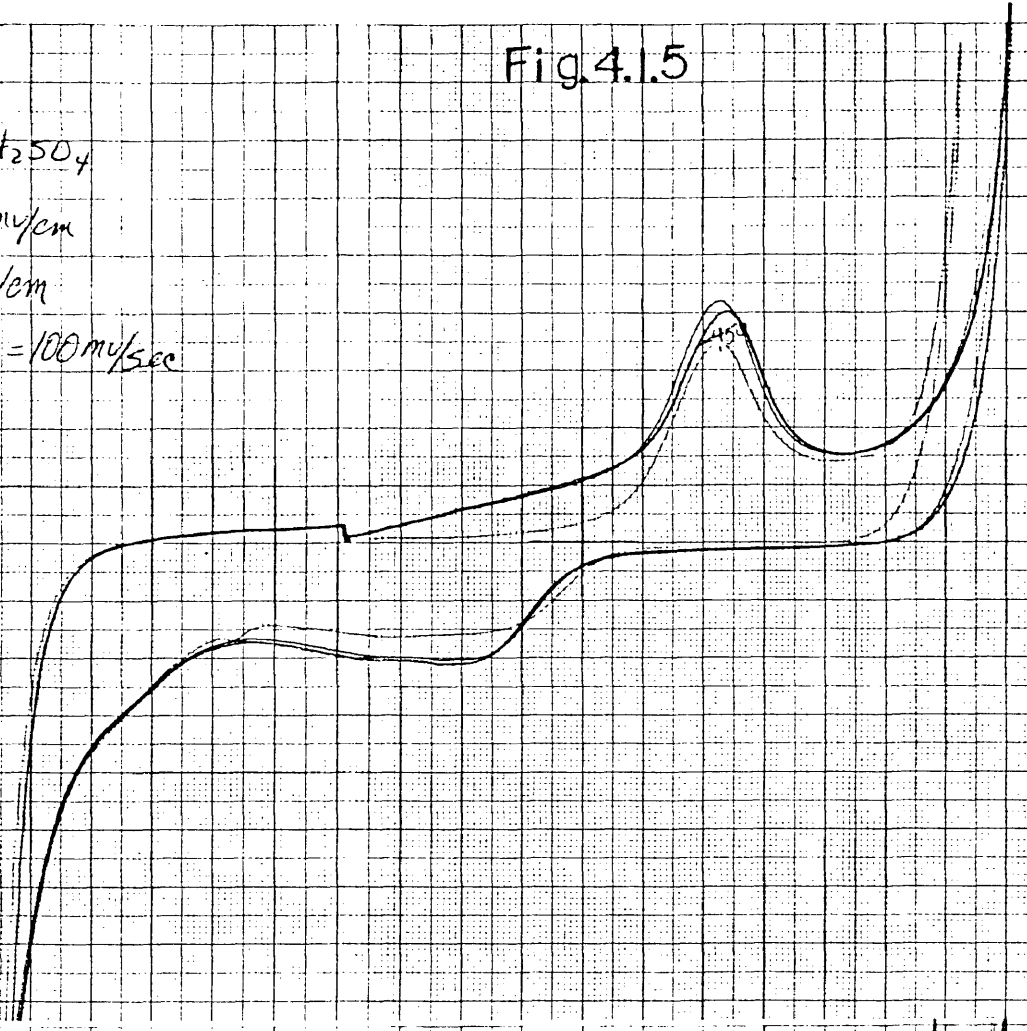


Fig.4.1.6

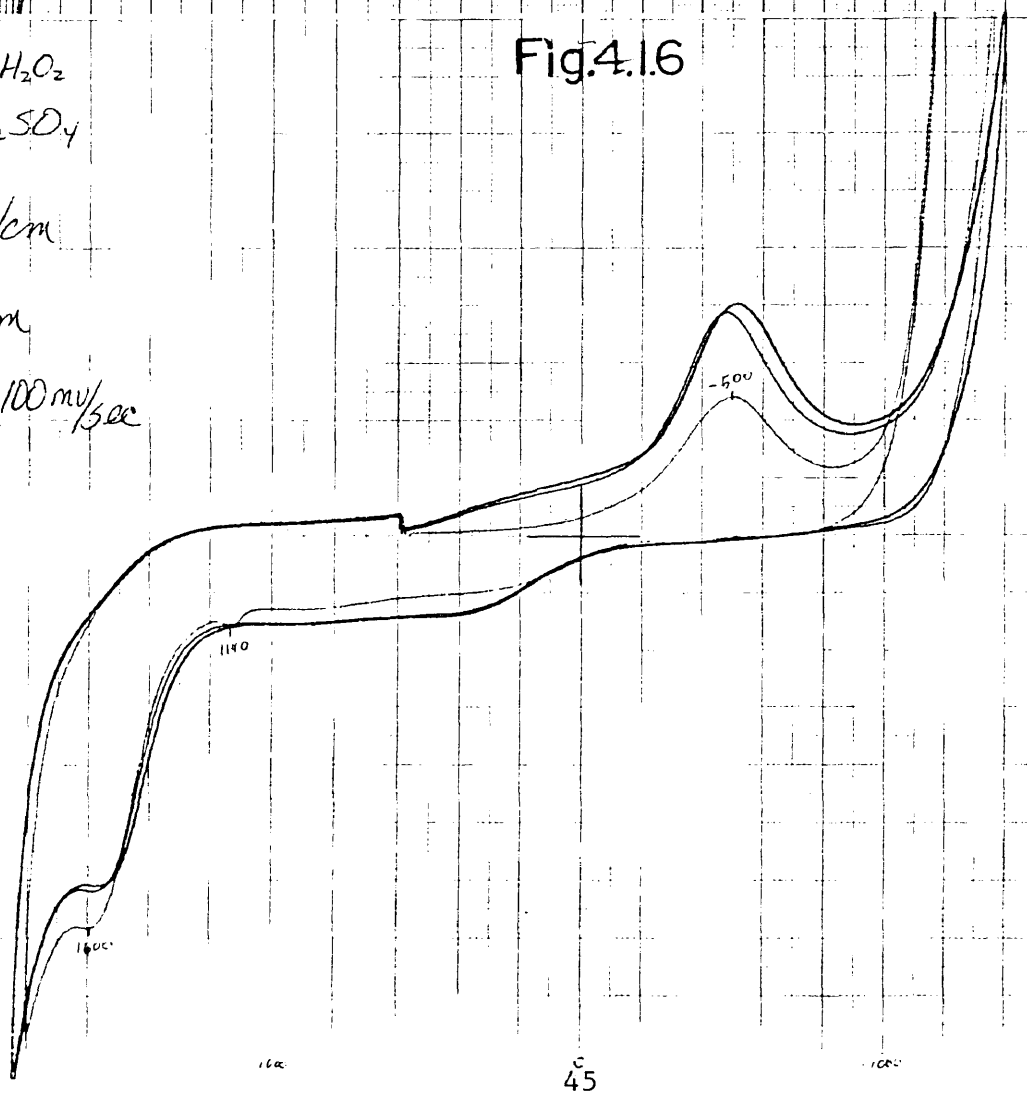
1.13×10^{-3} M H_2O_2

0.2M H_2SO_4

X = 200 mv/cm

Y = 10 μA/cm

Scan rate = 100 mv/sec



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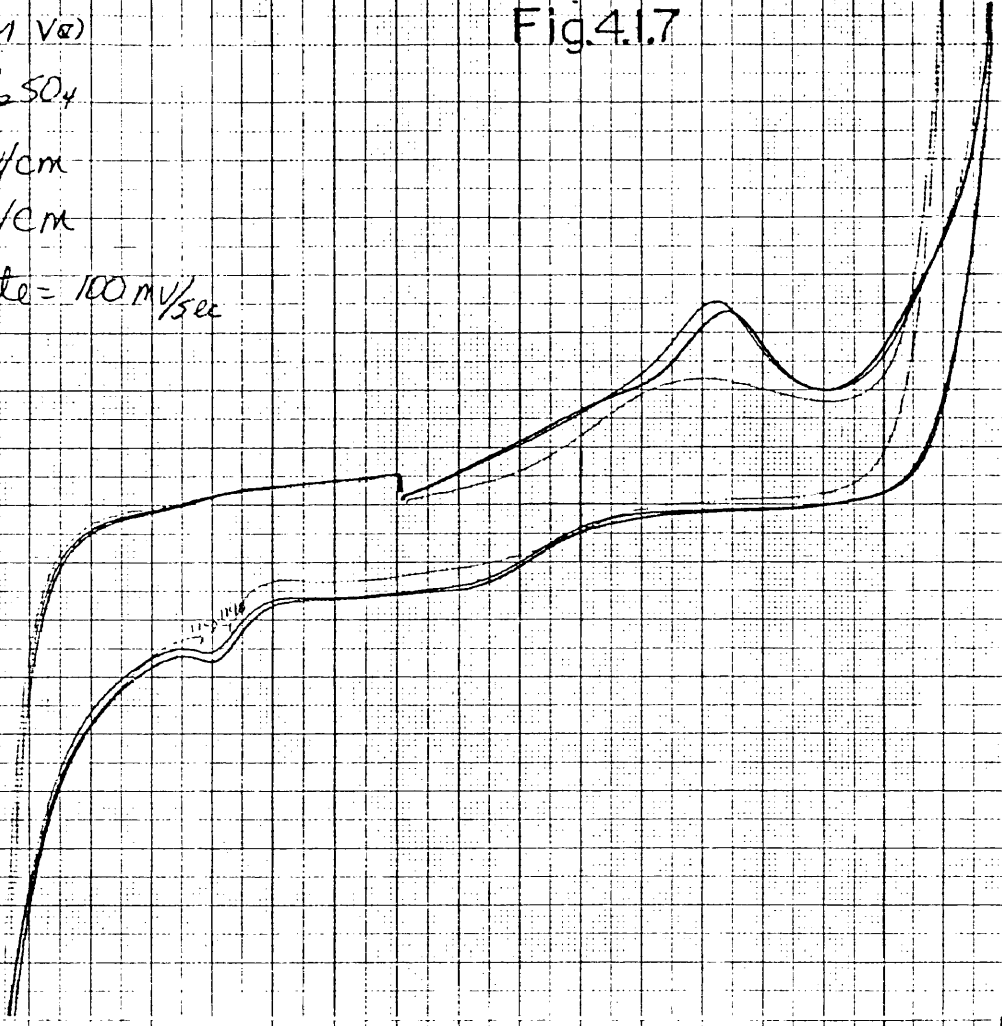
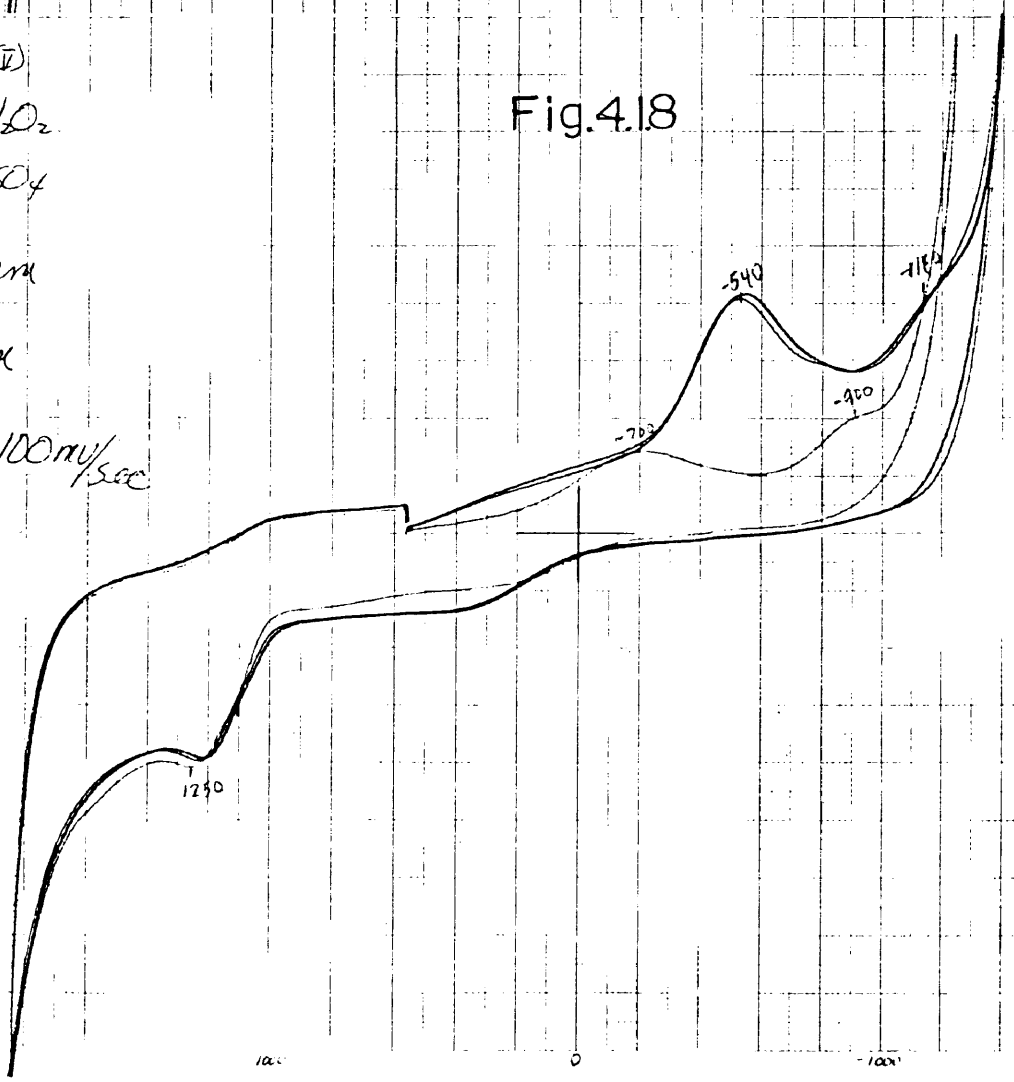
1.0×10^{-3} M V(Ⅴ)
0.2M H_2SO_4
X = 200mv/cm
Y = 10uA/cm
Scan rate = 100 mV/sec

Fig.4.1.7



1.0×10^{-3} M V(Ⅴ)
1.13×10^{-3} M H_2O_2
0.2M H_2SO_4
X = 200mv/cm
Y = 10uA/cm
Scan rate = 100mv/sec

Fig.4.1.8



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4.2 PEROXOVANADATES (V) IN THE PRESENCE OF HETEROLIGANDS

To study the electrochemistry of peroxovanadates in the presence of heteroligands, voltammograms shown in figures 4.1.3, 4.1.4, 4.1.7, 4.1.8, 4.3.1, 4.3.2, 4.4.6, 4.4.7, 4.5.5, 4.5.6, 4.6.4, 4.6.5, 4.7.3, 4.7.4, 4.8.3, and 4.8.4 were taken. Three cycles are shown (curves 1, 2 and 3). The initial starting potentials were between 500 and 600mV and initial scans were cathodic (except where indicated otherwise).

From the cyclic voltammograms of the various systems and the plots of the peak potentials, the following observations are made:

1) On comparing the cyclic voltammograms of peroxovanadates (V) in the presence of hydroxy-polycarboxylato heteroligands in 0.2M$LiClO_4$ (pH near 2.4), to peroxovanadates in the absence of heteroligands, one sees a significant difference in the number and position of peaks. One also notices a significant difference in the number and position of peaks between the voltammograms of the various hydroxy-polycarboxylato ligands (see the plots in figures 4.2.1 and 4.2.2). This information indicates that these heteroligands

have a significant effect on peroxo- vanadates present under these conditions and that the nature of the effect is dependent upon the heteroligand present.

2) On comparing the effect of the amino-polycarboxylato ligands NTA and EDTA on peroxovanadates in 0.2M$LiClO_4$, one sees many similarities and some differences in the number and position of peaks present to those present for peroxovanadates alone. The differences occur mainly on the anodic scan (see figures 4.2.1 and 4.2.2). Also the nature of the effect on the peroxo-vanadate does not appear to be as dependent upon the individual heteroligand as was the case with the hydroxy- polycarboxylato ligands. This information indicates that the amino-polycarboxylato heteroligands NTA and EDTA do not have as significant an effect on the peroxovanodates present under these conditions and time frame as do the hydroxy-polycarboxylato ligands.

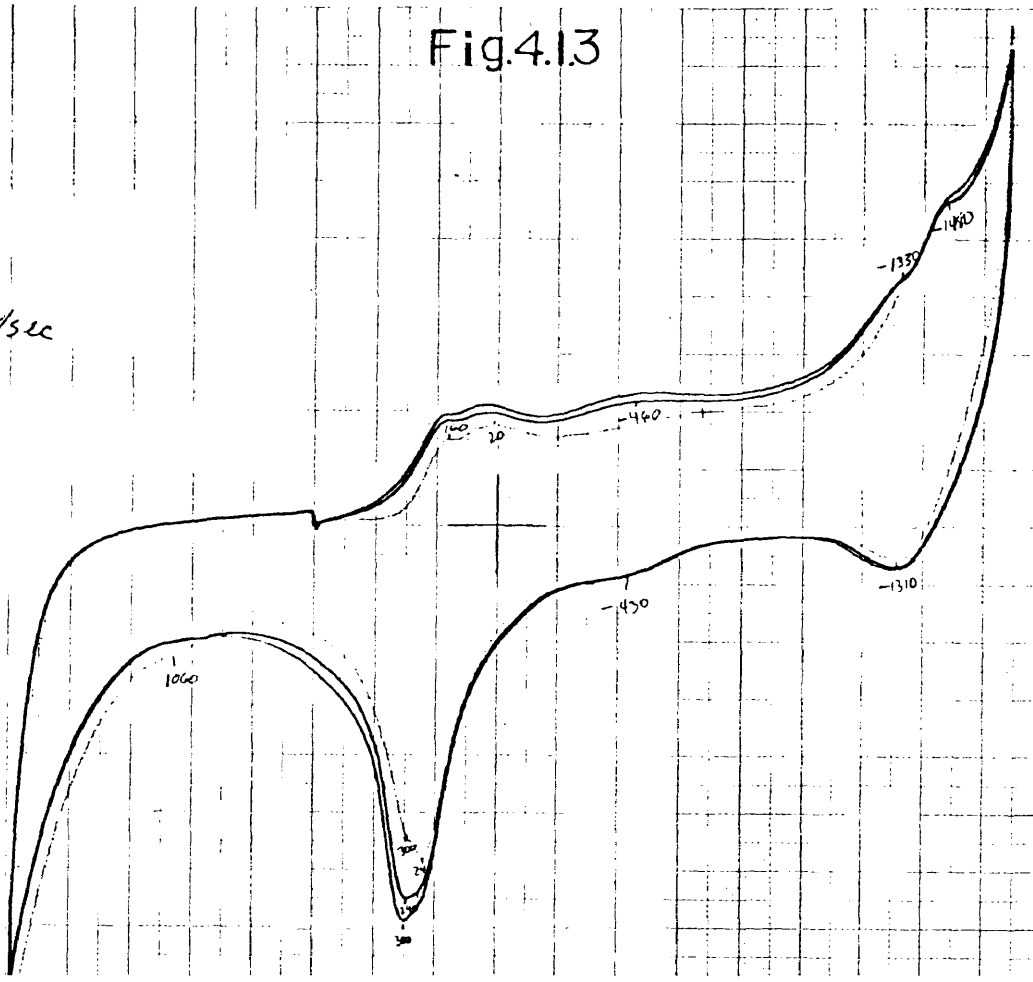
3) On comparing the voltammograms of the peroxovanadium hydroxy-polycarboxylato systems in 0.2MH_2SO_4 to peroxovanadates in the absence of heteroligands, one sees mainly similarities in the number and position of peaks (see the plot in figure 4.2.3). The one exception is the oxalato ligand. Apparently, under the conditions of high acidity the tarato, malato and citrato ligands do not have a significant effect on the peroxovanadates present while the oxalato ligand does.

4) On comparing the effect of the NTA and EDTA ligand on peroxovanadates present in $0.2MH_2SO_4$ to peroxovanadates alone one sees a considerable difference in the peaks present. The nature of the effect appears to be somewhat similar for the NTA and EDTA ligands. These results imply that the peroxovanadates present under these conditions and time frame are effected to some similar extent by the presence of NTA and EDTA.

Fig.4.13

1.0×10^{-3}M V(II)
0.2M $LiClO_4$

X = 200mV/cm
Y = 5μA/cm
Scan rate = 100mV/sec



pH = 3.34

Fig.4.14

1.9×10^{-3}M V(II)
1.08×10^{-3}M H_2O_2
0.2M $LiClO_4$

X = 200mV/cm
Y = 10μA/cm
Scan rate = 100mV/sec

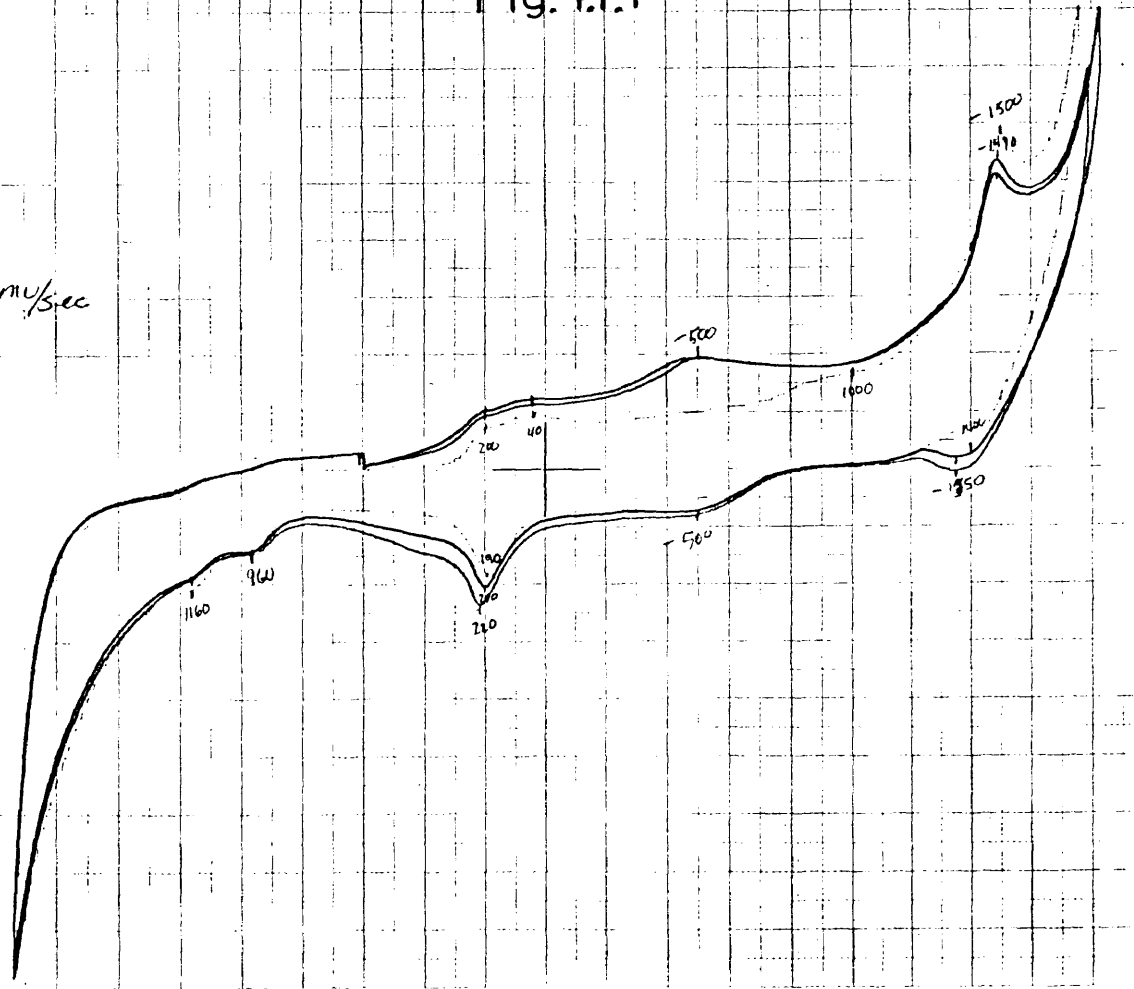


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Fig.4.1.7

1.0×10^{-3} M V(II)

0.2M H_2SO_4

X = 200 mv/cm

Y = 10 uA/cm

Scan rate = 100 mV/sec

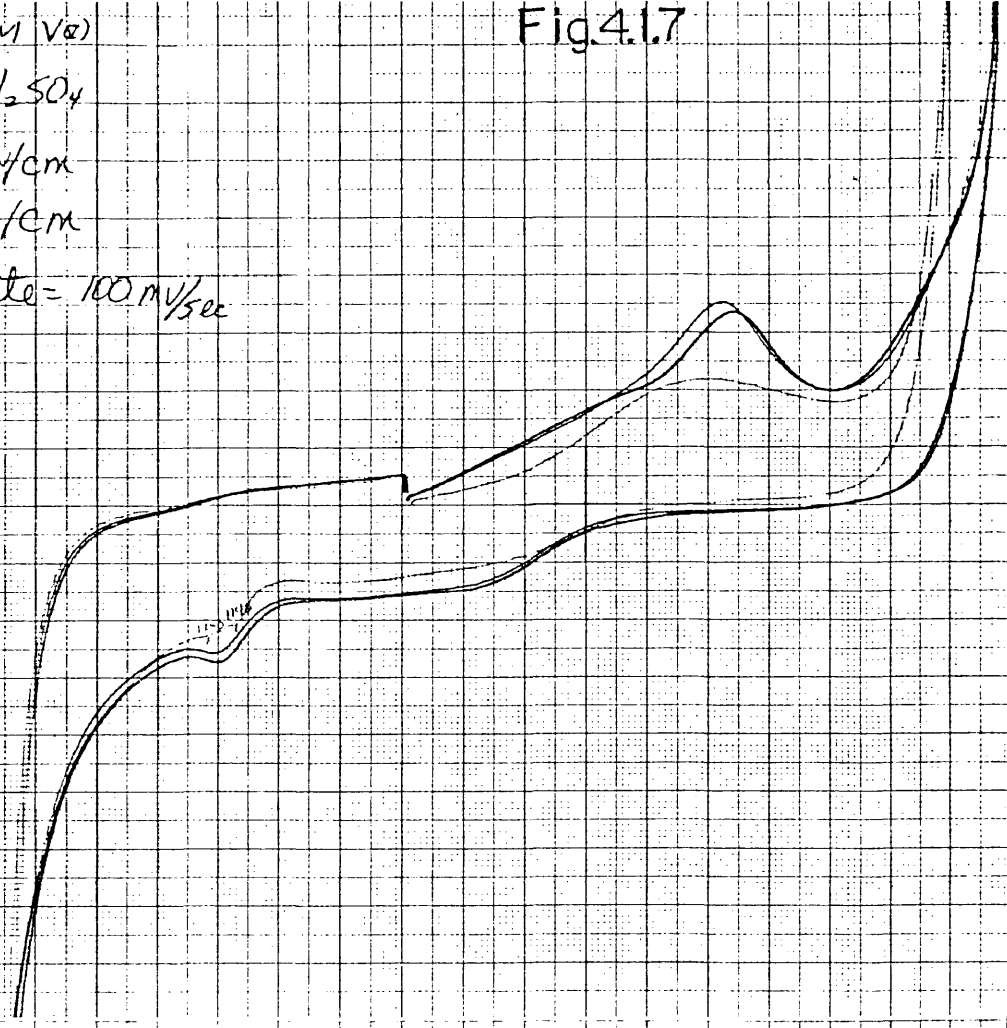

Fig.4.18

1.0×10^{-3} M V(V)

1.13×10^{-3} M H_2O_2

0.2M H_2SO_4

X = 200 mv/cm

Y = 10 uA/cm

Scan rate = 100 mv/sec

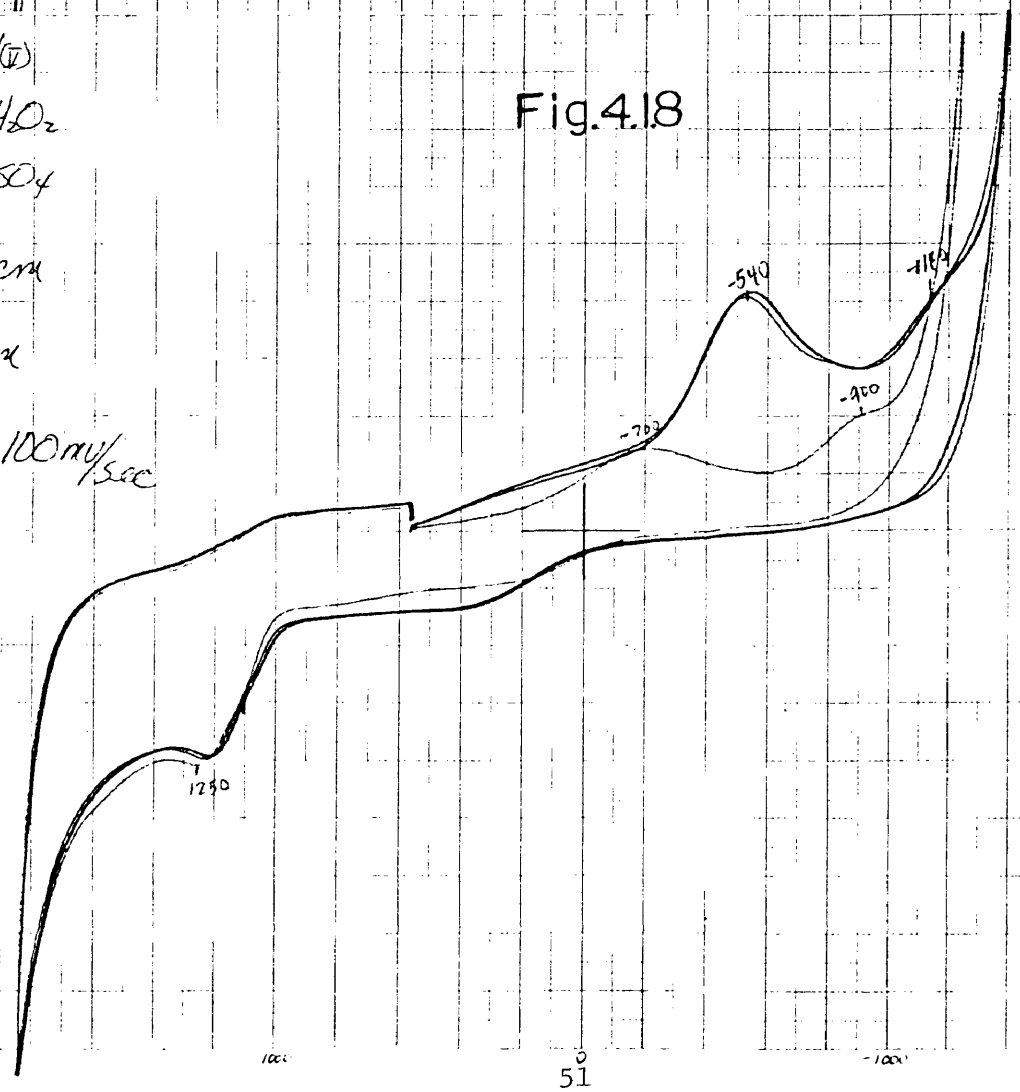

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Fig.4.3.1

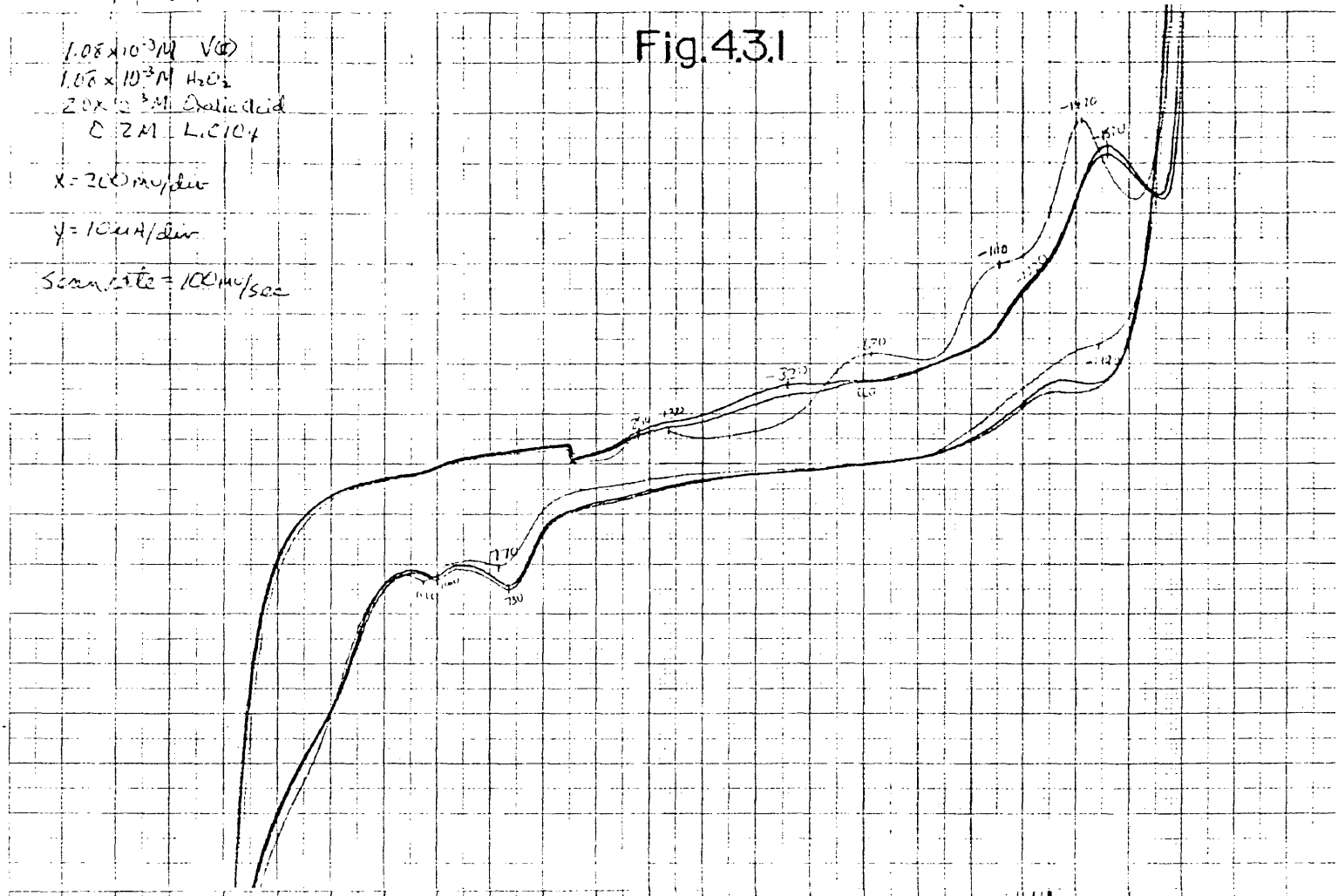
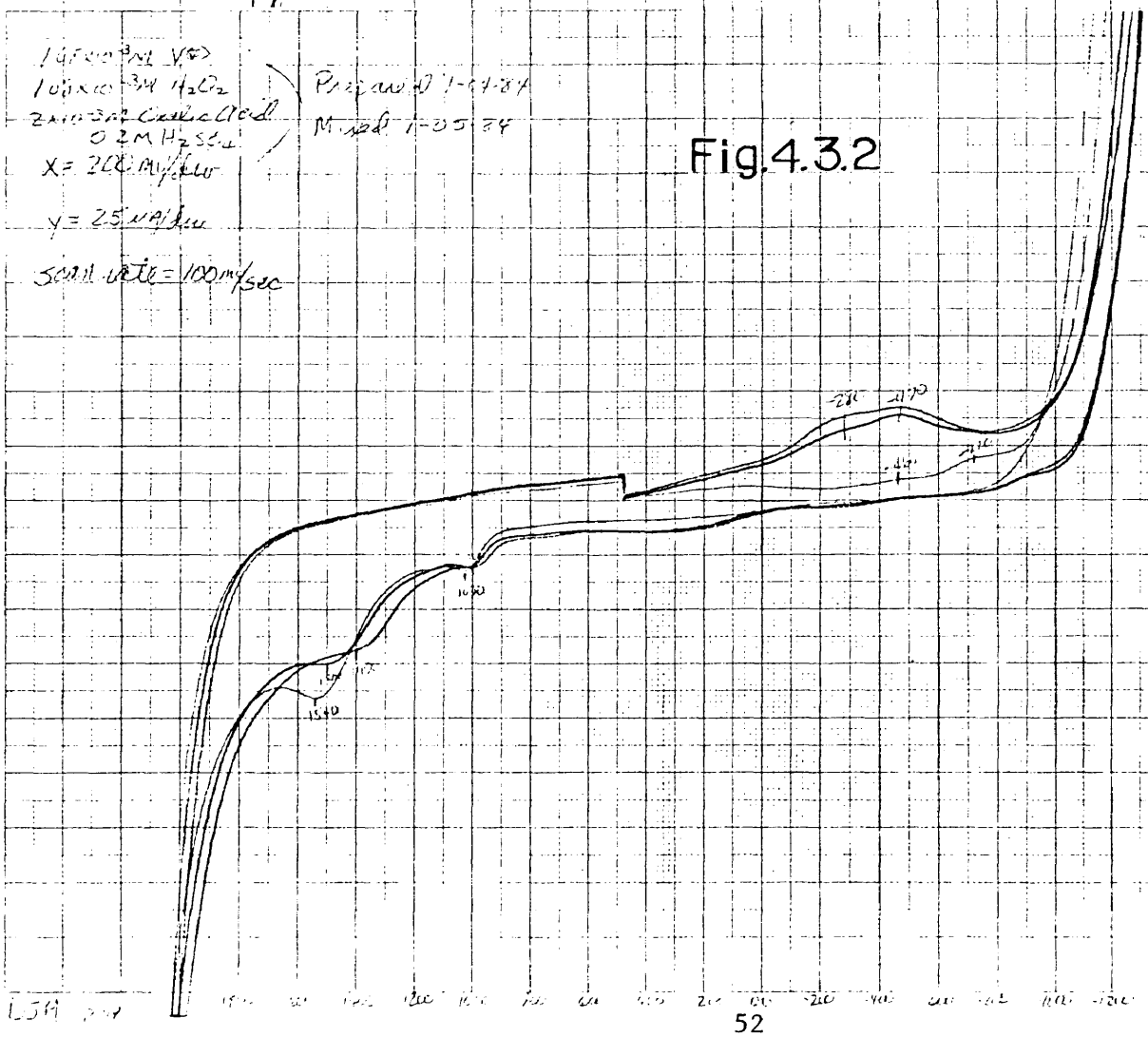


Fig.4.3.2



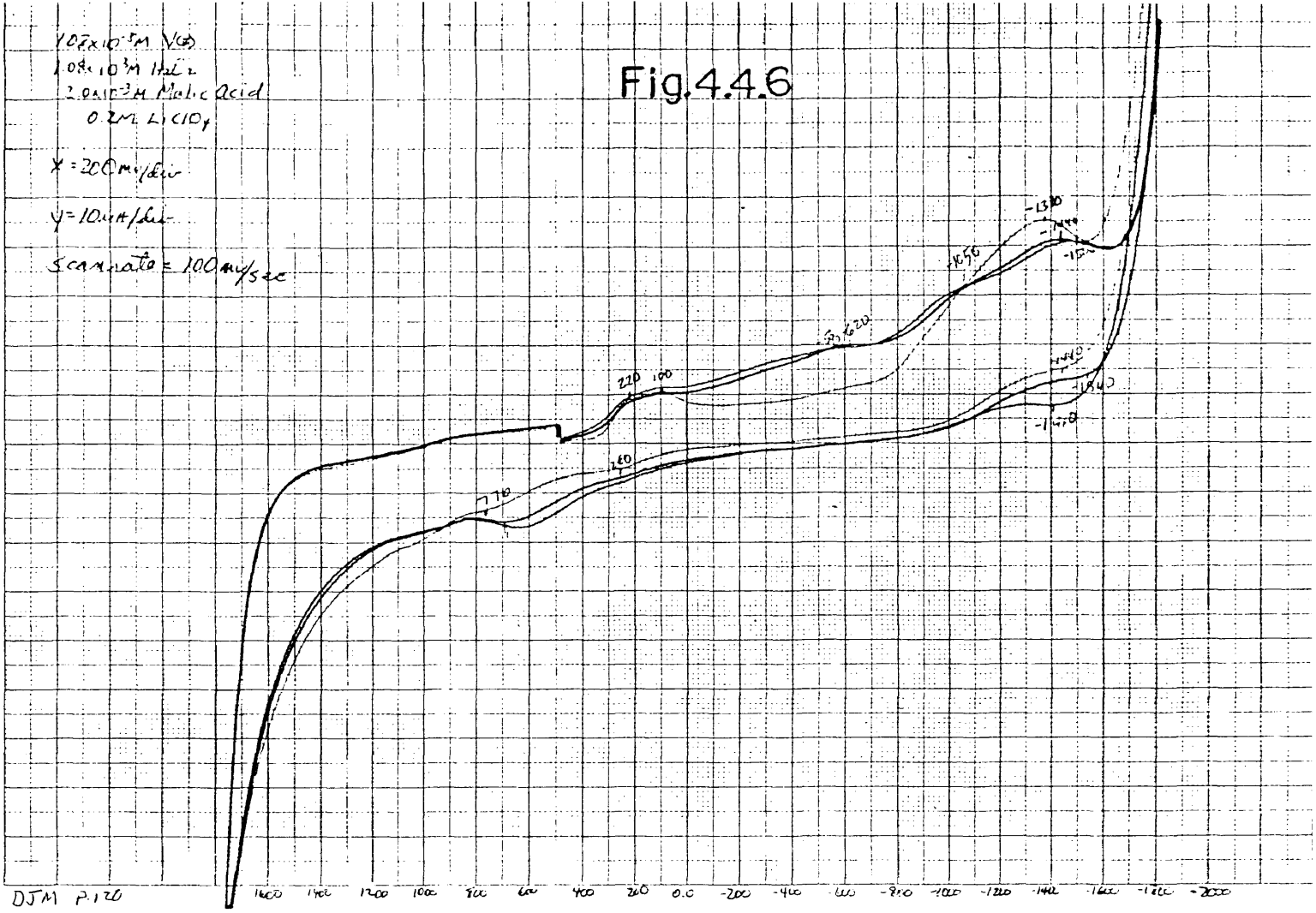
10.2×10^{-5}M VO^{2+}
1.08×10^{-3}M H_2SO_4
2.0×10^{-3}M Malic Acid
0.2M $LiClO_4$

X = 200mv/div

Y = 10uA/div

Scan rate = 100mv/sec

Fig.4.4.6



DJM p.120
1-09-84

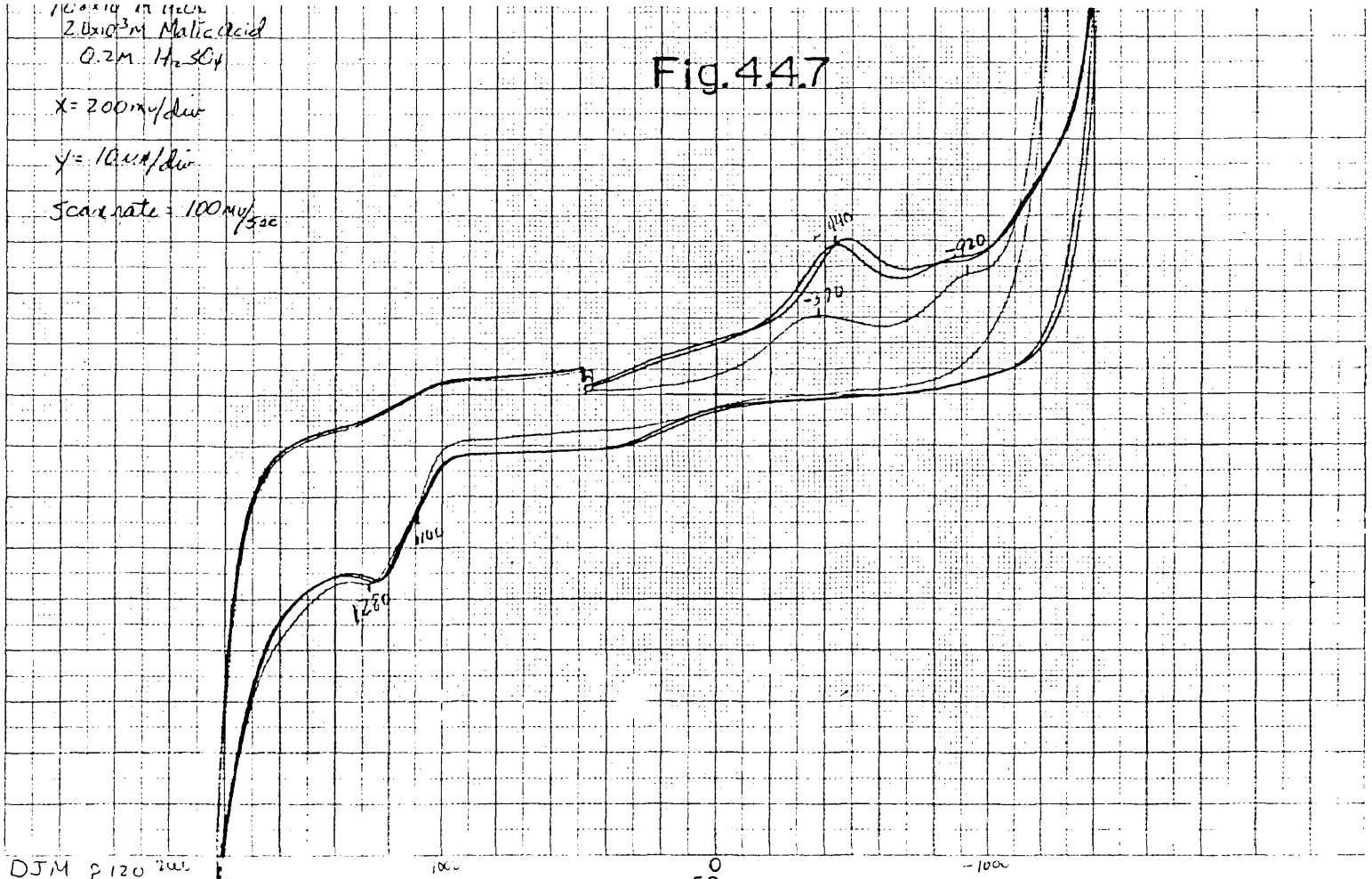
Fig.4.4.7

2.0×10^{-3}M Malic Acid
0.2M H_2SO_4

X = 200mv/div

Y = 10uA/div

Scan rate = 100mv/sec



DJM p.120
1-09-84

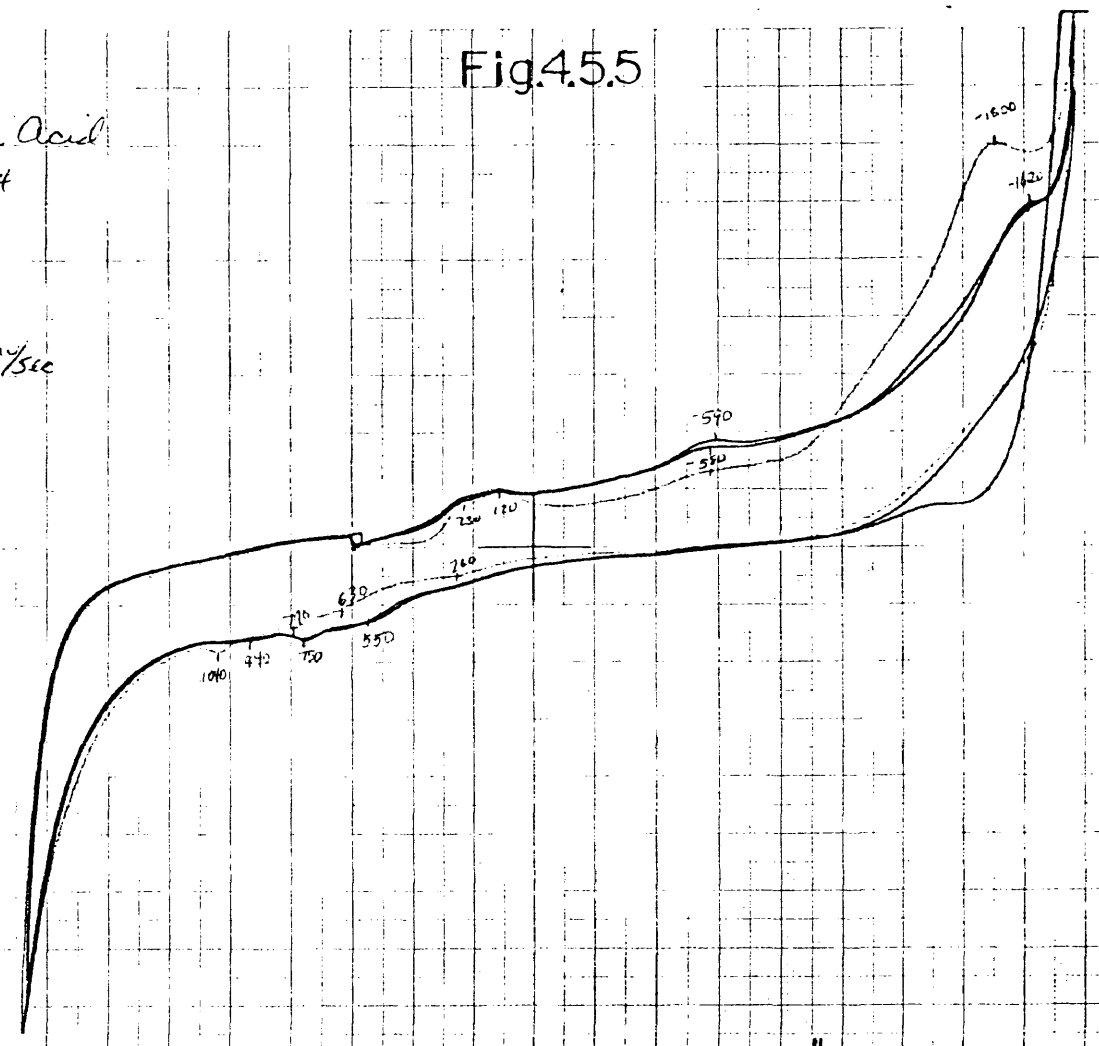
pH = 2.14
1.00×10^{-3}M V(V)
1.08×10^{-3}M H_2O_2
2.0×10^{-3}M Citric Acid
0.2M $LiClO_4$

X = 200mv/cm

Y = 10μA/cm

Scan rate = 100mv/sec

Fig.4.5.5



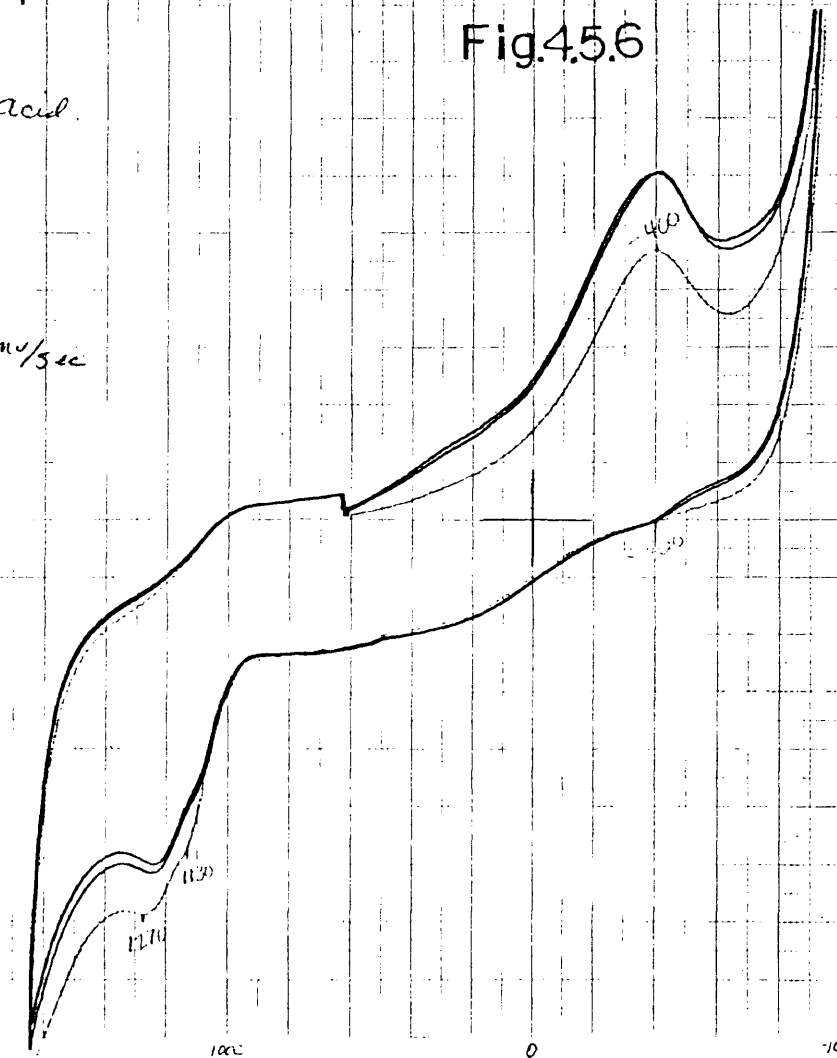
1.00×10^{-3}M V(V)
1.08×10^{-3}M H_2O_2
2.0×10^{-3}M Citric Acid
0.2M H_2SO_4

X = 200mv/cm

Y = 5μA/cm

Scan rate = 100mv/sec

Fig.4.5.6



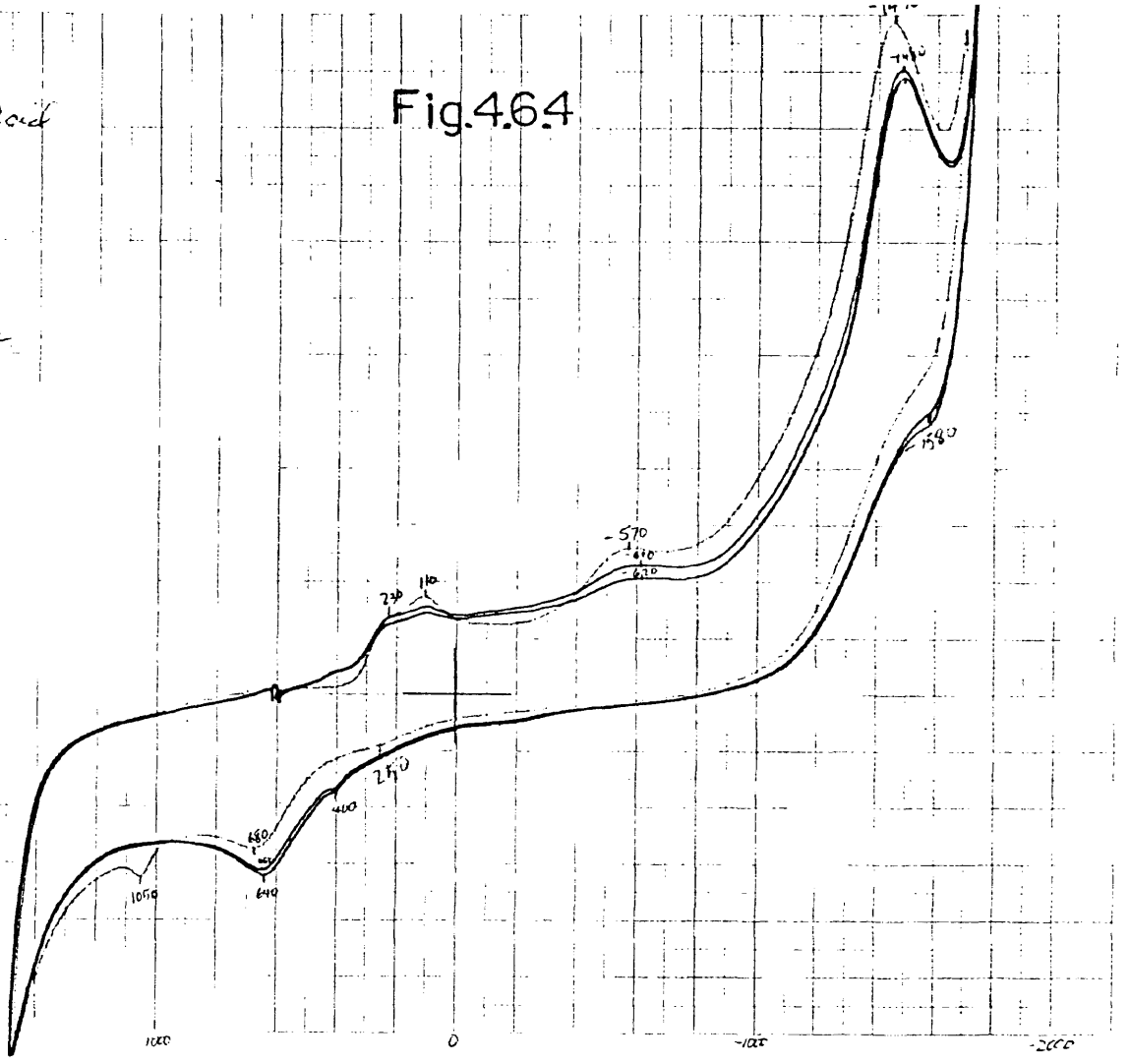
1.00×10⁻³M V(III)
1.08×10⁻³M H_2O_2
2.0×10⁻³M Tartaric Acid
0.2M $LiClO_4$

X = 200mV/cm

Y = 5μA/cm

Scan rate = 100mV/sec

Fig.4.6.4



DJM p.129
5-04-84

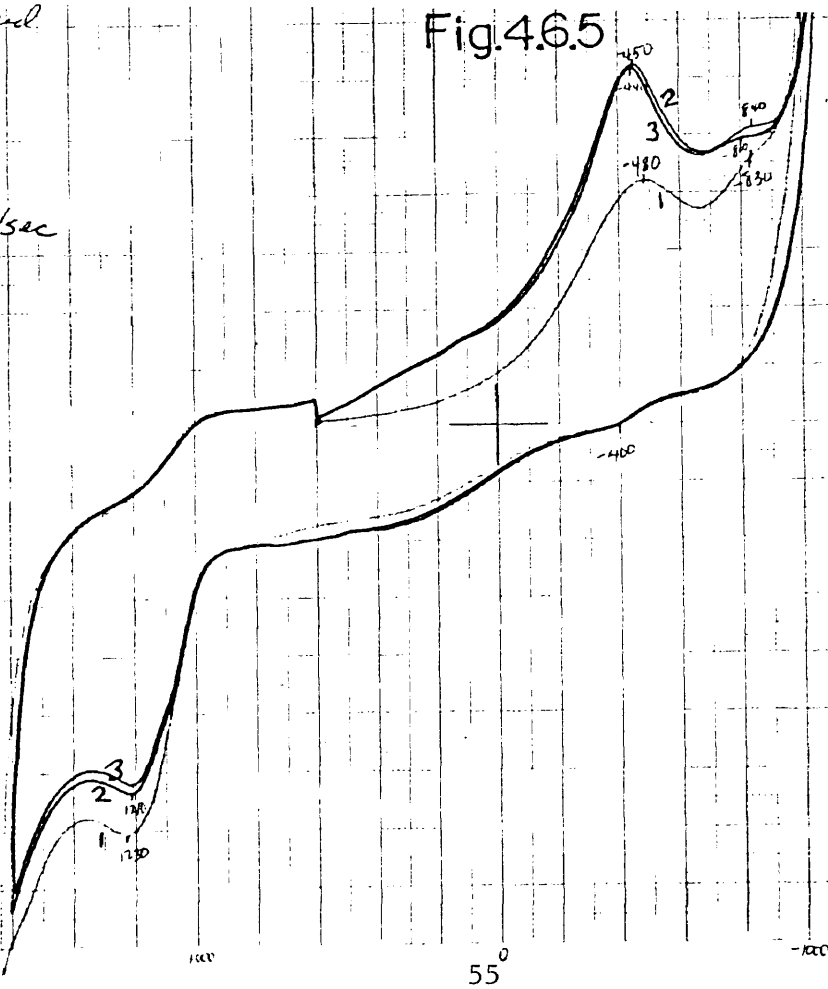
2.0×10⁻³M Tartaric Acid
0.2M H_2SO_4

X = 200mV/cm

Y = 5μA/cm

Scan rate = 100mV/sec

Fig.4.6.5



DJM p.126
5-04-84

Fig.4.7.3

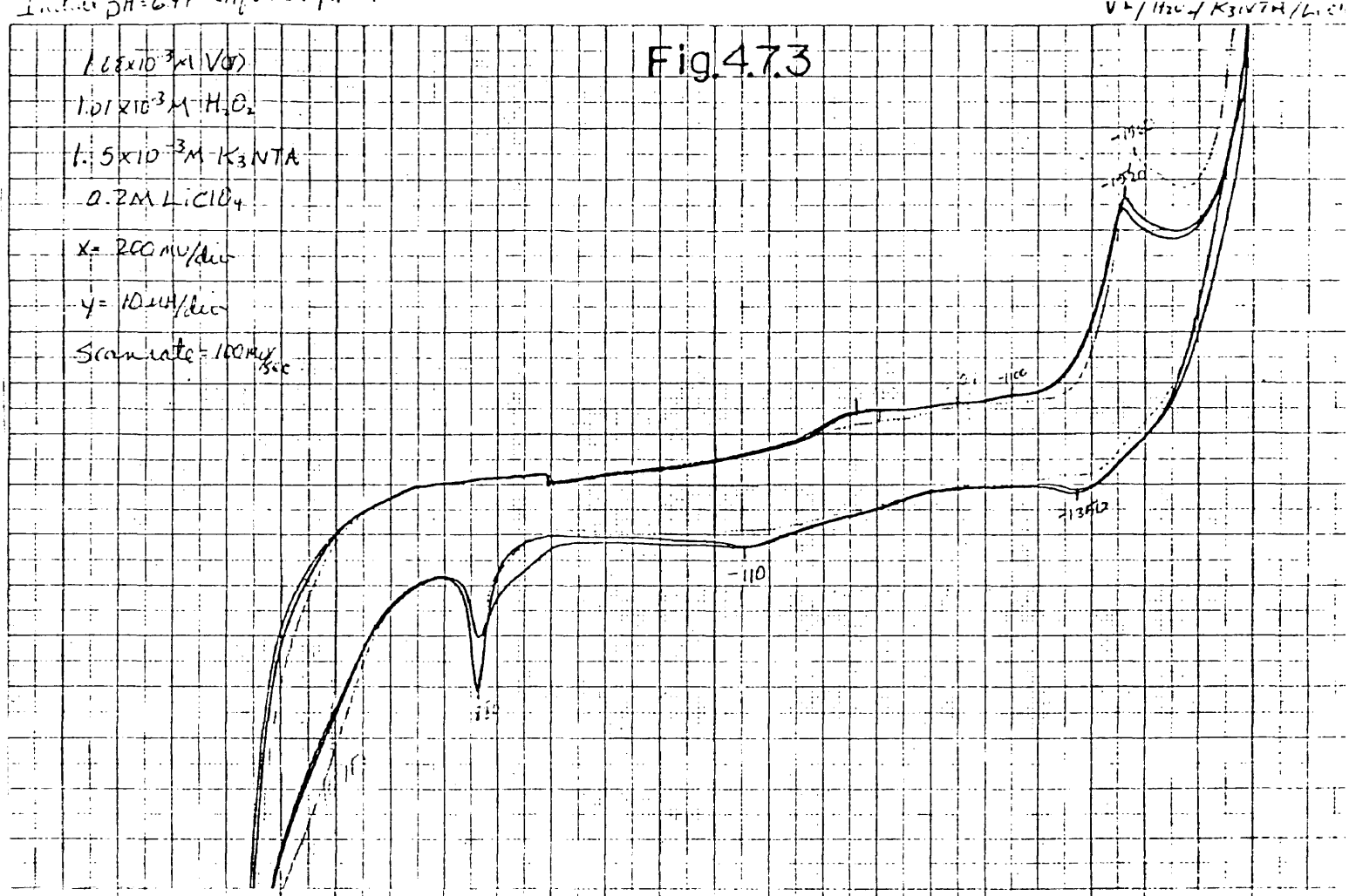
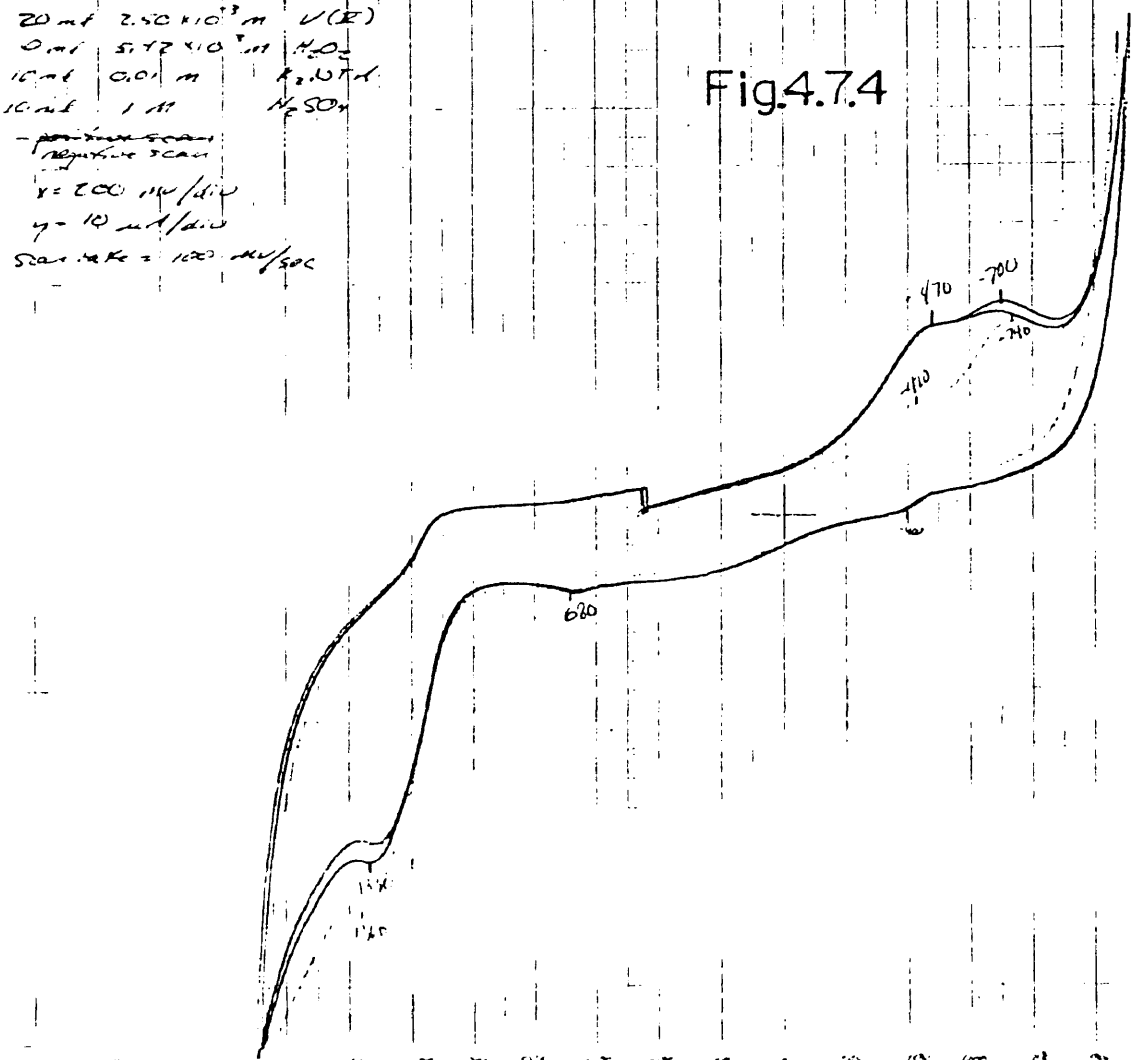


Fig.4.7.4



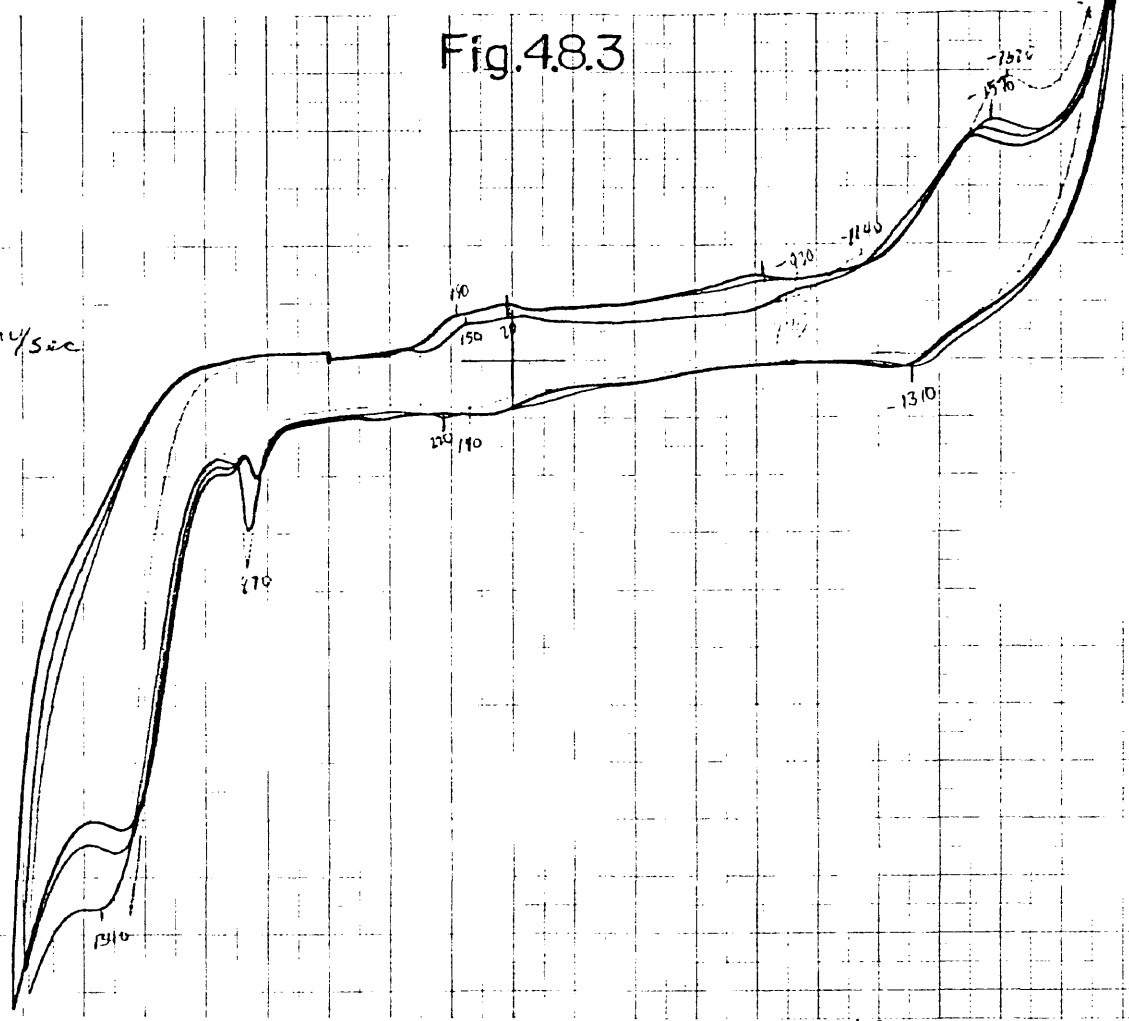
pH = 3.65
1.00×10^{-3}M V(V)
1.08×10^{-3}M H_2C_2
2.0×10^{-3}M EDTA
0.2M $LiClO_4$

X = 200 mv/cm

Y = 10 μA/cm

Scan rate = 100 mv/sec

Fig. 4.8.3



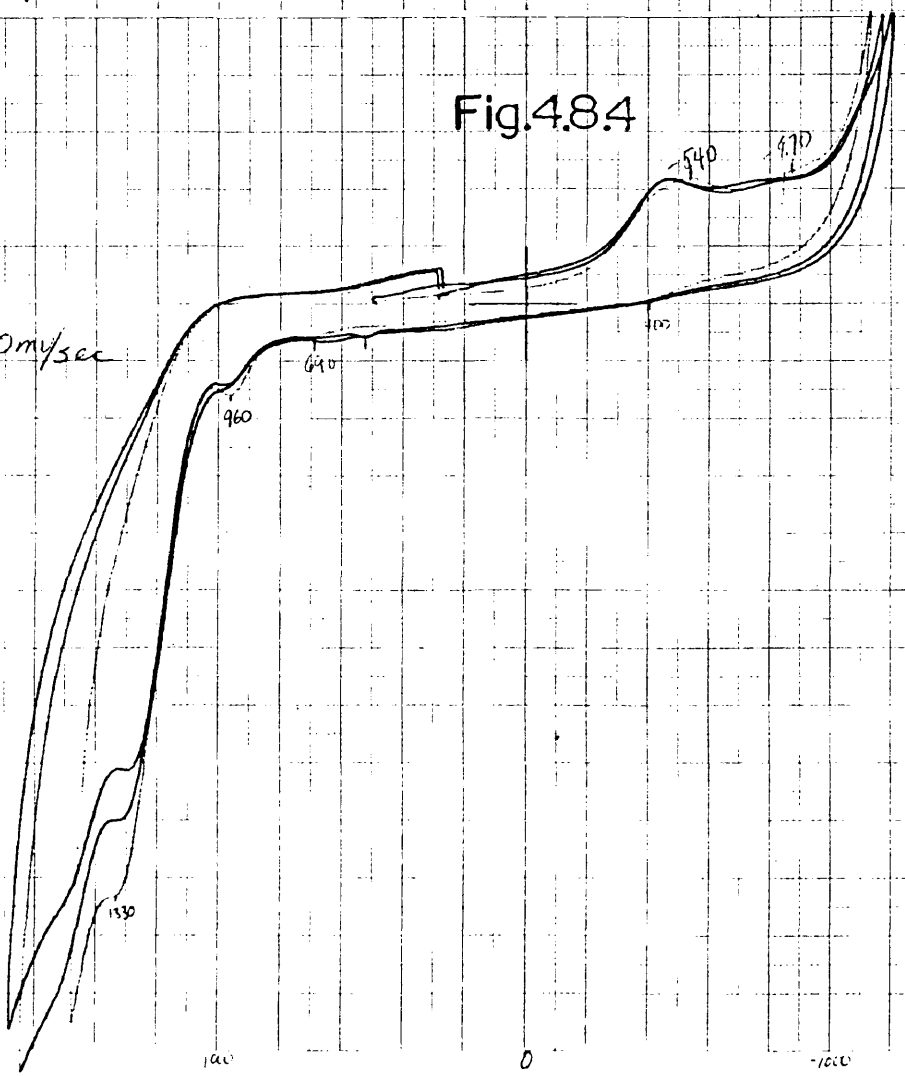
1.00×10^{-3}M V(V)
1.08×10^{-3}M H_2C_2
2.0×10^{-3}M EDTA
0.2M H_2SO_4

X = 200 mv/cm

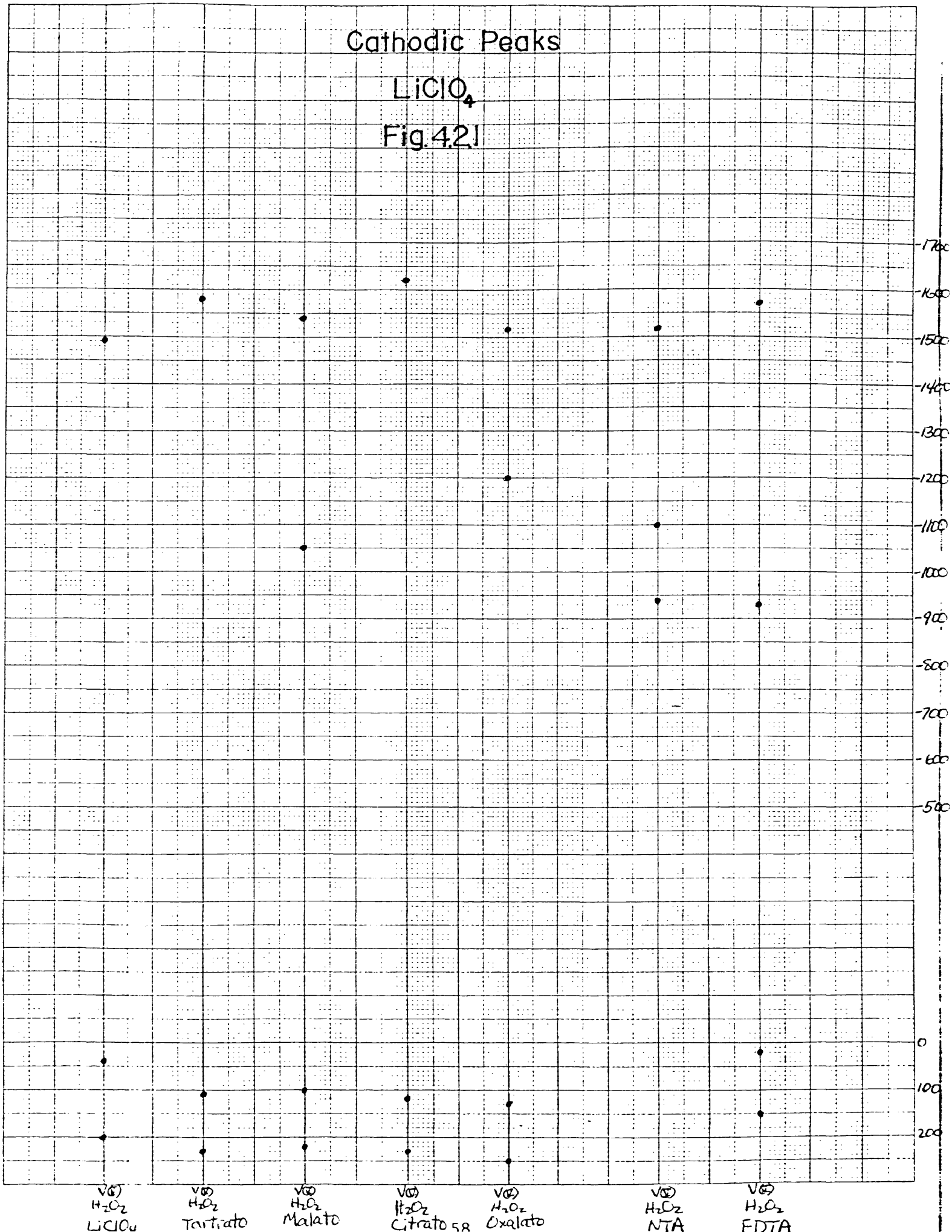
Y = 10 μA/cm

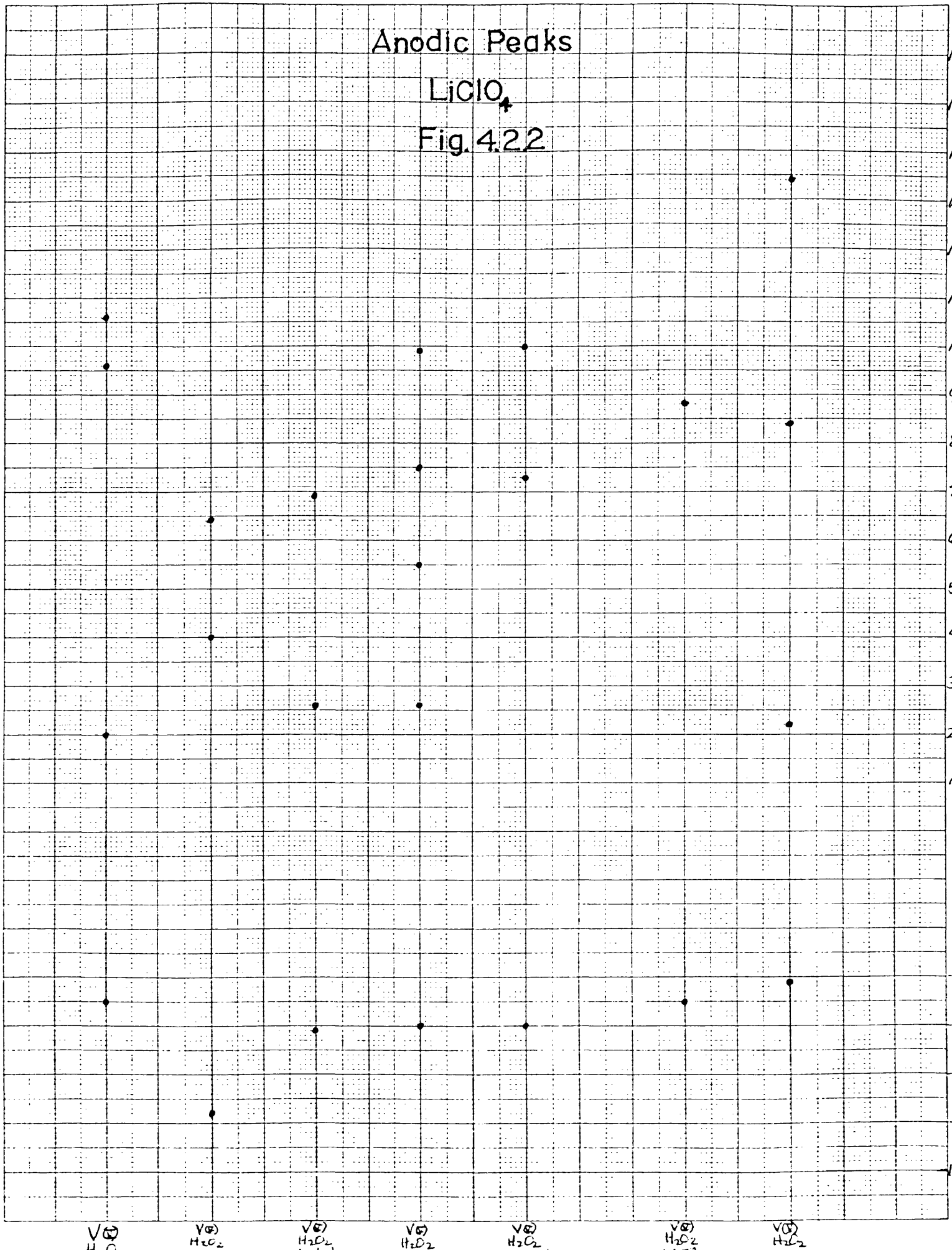
Scan rate = 100 mv/sec

Fig. 4.8.4



DJM p.129
5-04-84

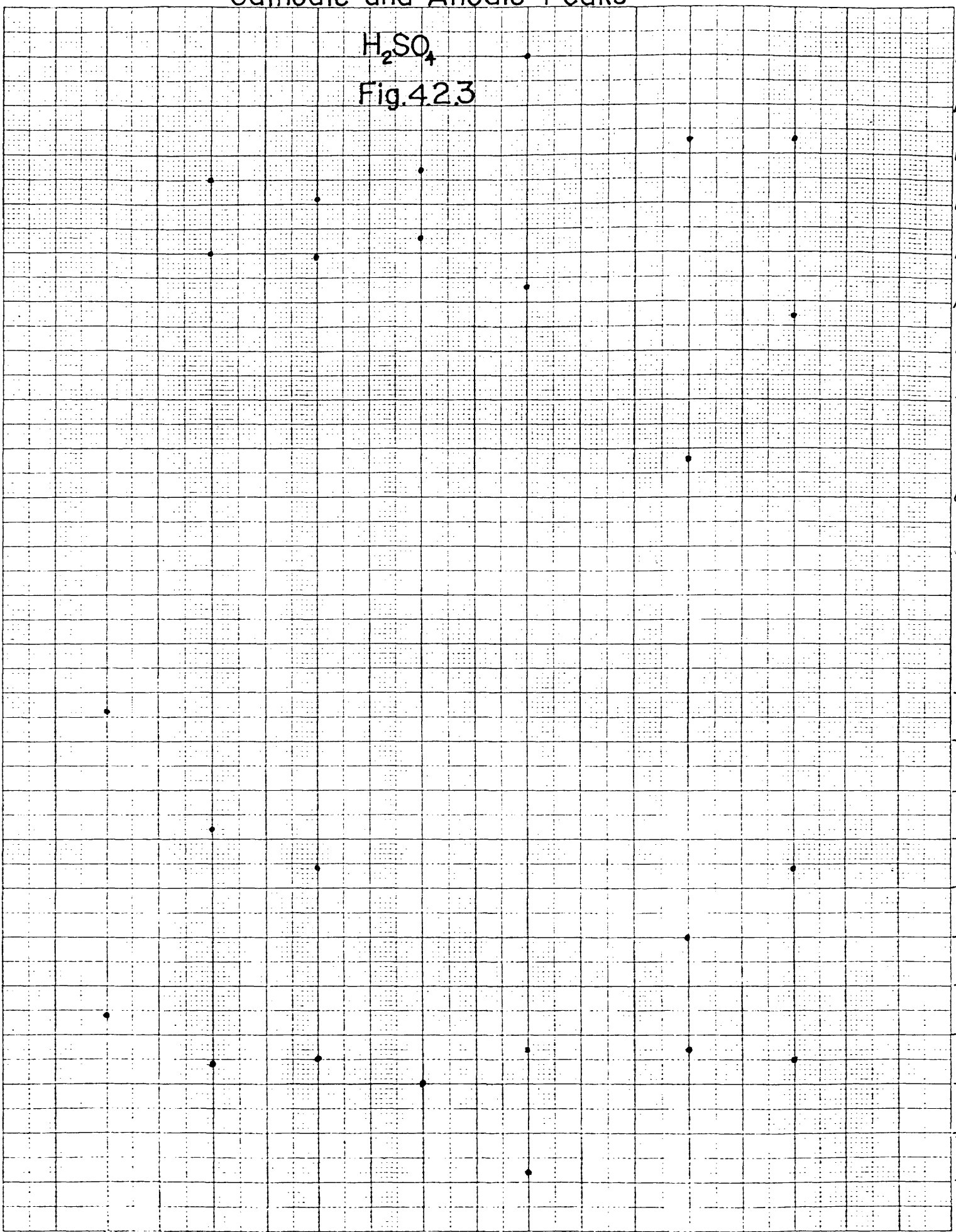

Cathodic Peaks
LiClO4
Fig. 4.21
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
0
100
200
V(s) H2O2 LiClO4
V(s) H2O2 Tartrato
V(s) H2O2 Malato
V(s) H2O2 Citrato
V(s) H2O2 Oxalato
V(s) H2O2 NTA
V(s) H2O2 EDTA


Anodic Peaks
LiClO4
Fig. 4.22
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
-130
-140
-150
-160
-170
V(E)
H2O2
V(E)
H2O2
V(E)
H2O2
Malate
V(E)
H2O2
V(E)
H2O2
V(E)
H2O2
NTA
V(E)
H2O2
EDTA

Cathodic and Anodic Peaks

H_2SO_4

Fig. 4.2.3



4.3 PEROXO OXALATO VANADATES (V)

The compound $K_3[VO(o)_2)_2$oxalato$]\cdot 2H_2O$[20] has been prepared and characterized (section 2.3). To study the electrochemistry of vanadium(V) in analogous systems, voltammograms shown in figures 4.1.1 through 4.1.8 and 4.3.1 through 4.3.4 were taken. Three cycles are shown (curves 1, 2 and 3). The starting potential was near 550mV and initial scans were cathodic (except where otherwise indicated).

From the cyclic voltammograms of the various systems, the plots of the peak potentials, and the potentiometric titrations, the following observations are made:

1) The effect of the oxalato ligand on peroxovanadium(V) species in 0.2M $LiClO_4$ can be observed by comparing figures 4.3.1 and 4.1.4. One immediately notices the additional cathodic peaks present on the first cycle and the disappearance of the anodic peaks near 200mV when the oxalato ligand is present. Also the two anodic peaks near 1000mV have been shifted toward more negative potentials while the vanadium (V/IV) peaks near 200 and 50mV have been shifted toward more positive potentials (see fig. 4.3.5). There is also the appearance

of a shoulder on the anodic scan near 1400mV. These results indicate that the oxalato ligand has a significant effect on the peroxovanadium(V) species present under these conditions and time frame.

2) The effect of the oxalato ligand on peroxovanadium(V) species in 0.2M H_2SO_4 can be seen by comparing figures 4.3.2 and 4.1.8. The outstanding features of this comparison appear to be the shift of all peak potentials toward more positive potentials and the addition of an anodic peak near 100mV. These results indicate that the Oxolato ligand has a significant effect on the peroxovanadium(V) species present at this low pH.

3) On comparing the effect of the background electrolyte on the electroactive species present, one sees fewer peaks for the system in acid (fig. 4.3.2) than at a pH=2.61 (fig. 4.3.1). As before, this is expected considering the effect of pH on vanadium(V) species in aqueous solution.

4) The potentiometric titrations show good agreement in the stoichiometry and the reproducibility of the potentials measured at characteristic points (i.e. the starting potential, half-points, inflections, etc.) for cesium and ammonium salts.

The compounds did not behave like the mixture of components in acid solution.

Fig.4.3.1

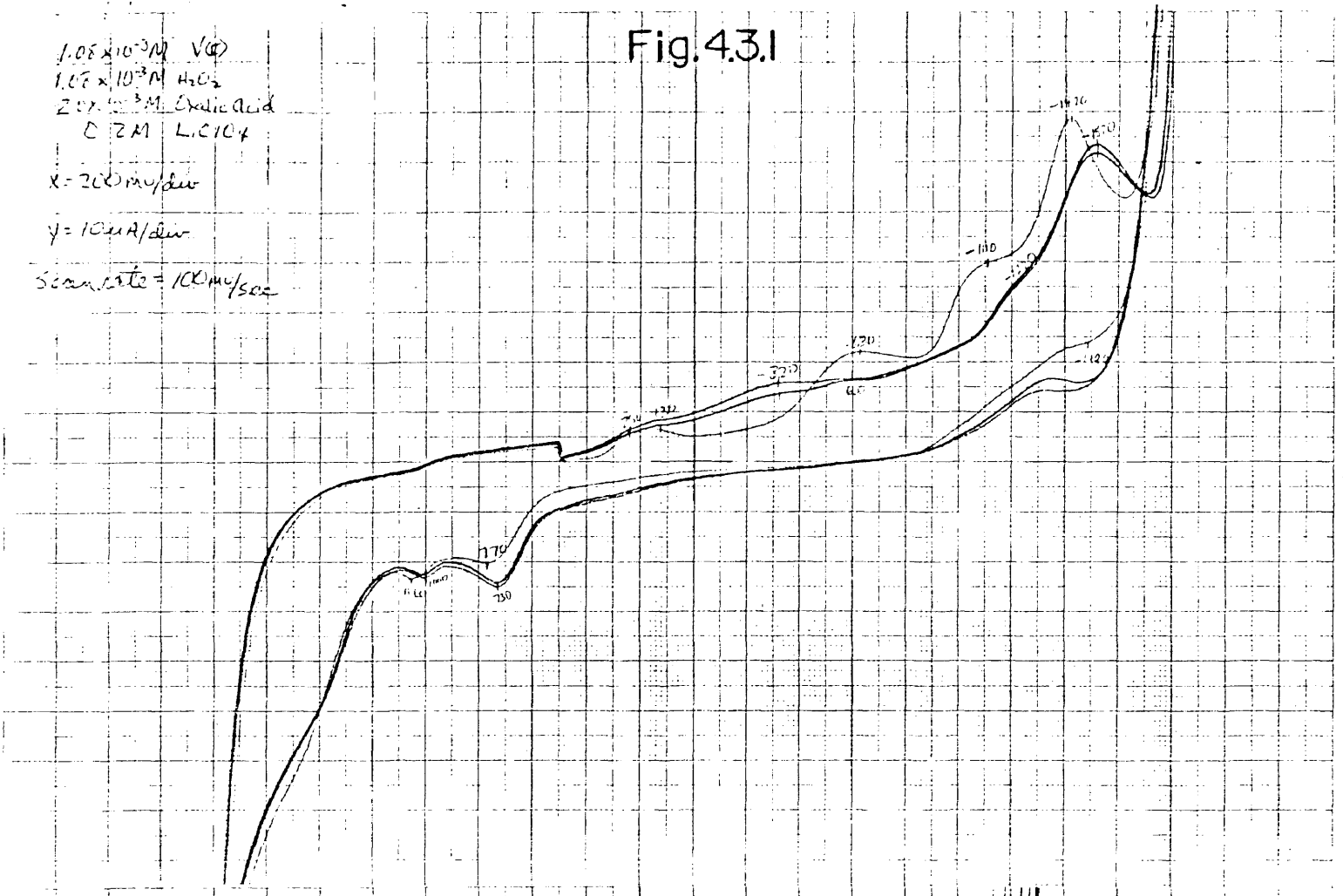
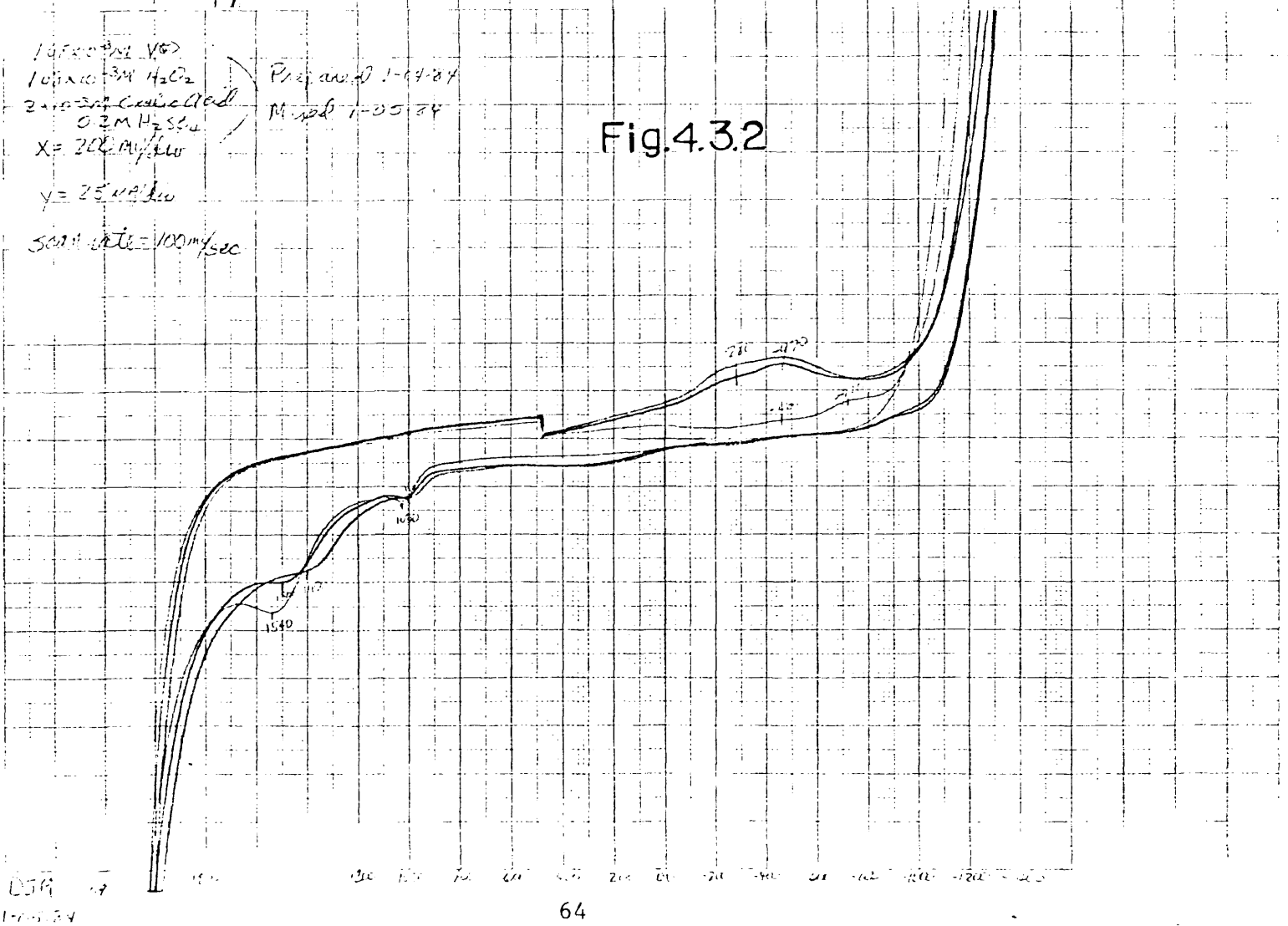


Fig.4.3.2



pH = 2.63

2.0×10^{-3}M Oxalic Acid

0.2M $LiClO_4$

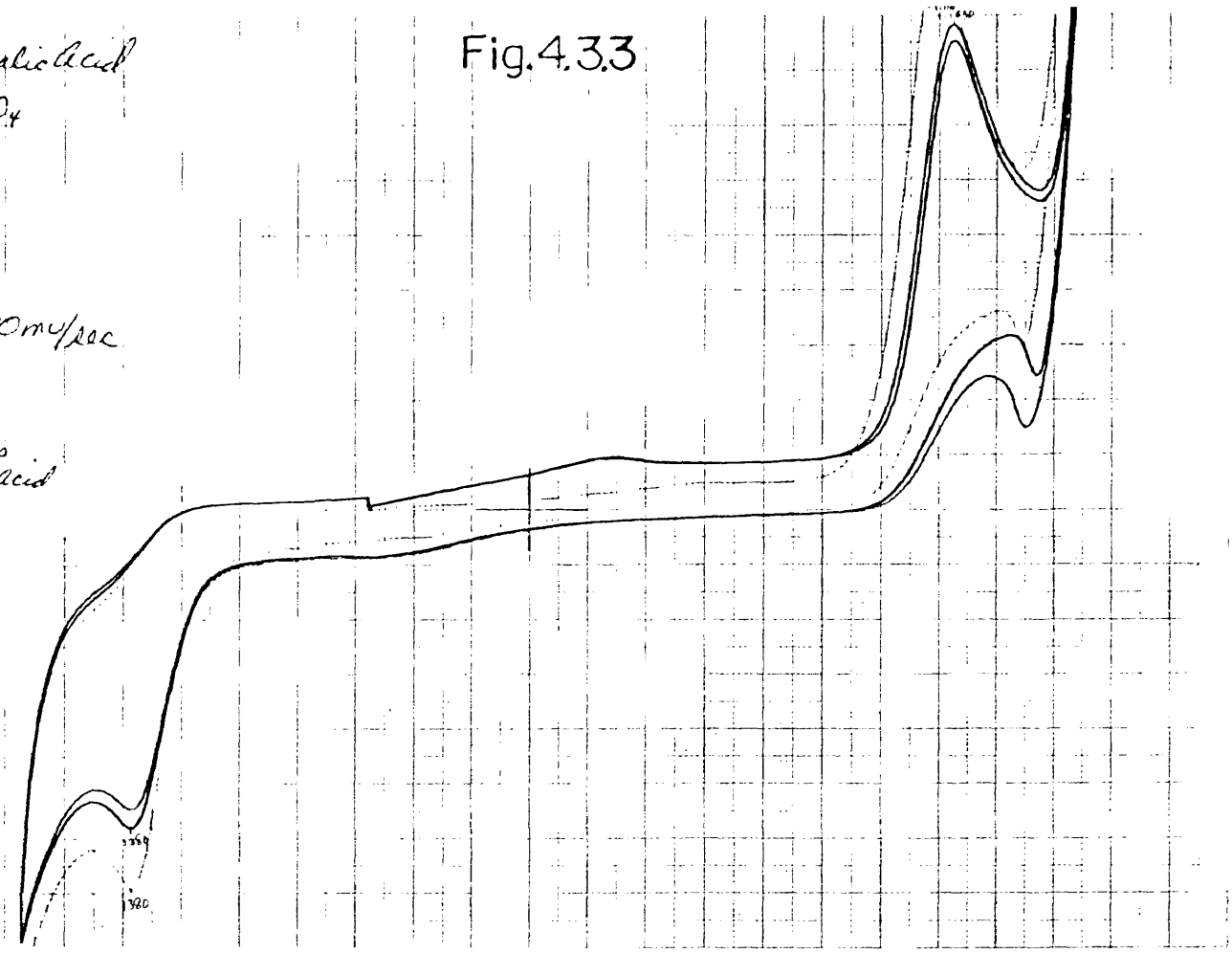
x = 200mv/cm

y = 10uA/cm

Scan rate = 100mv/sec

Blank $LiClO_4$ was run with Citric Acid

Fig. 4.3.3



pH = 2.63

2.0×10^{-3}M Oxalic Acid

0.2M $LiClO_4$

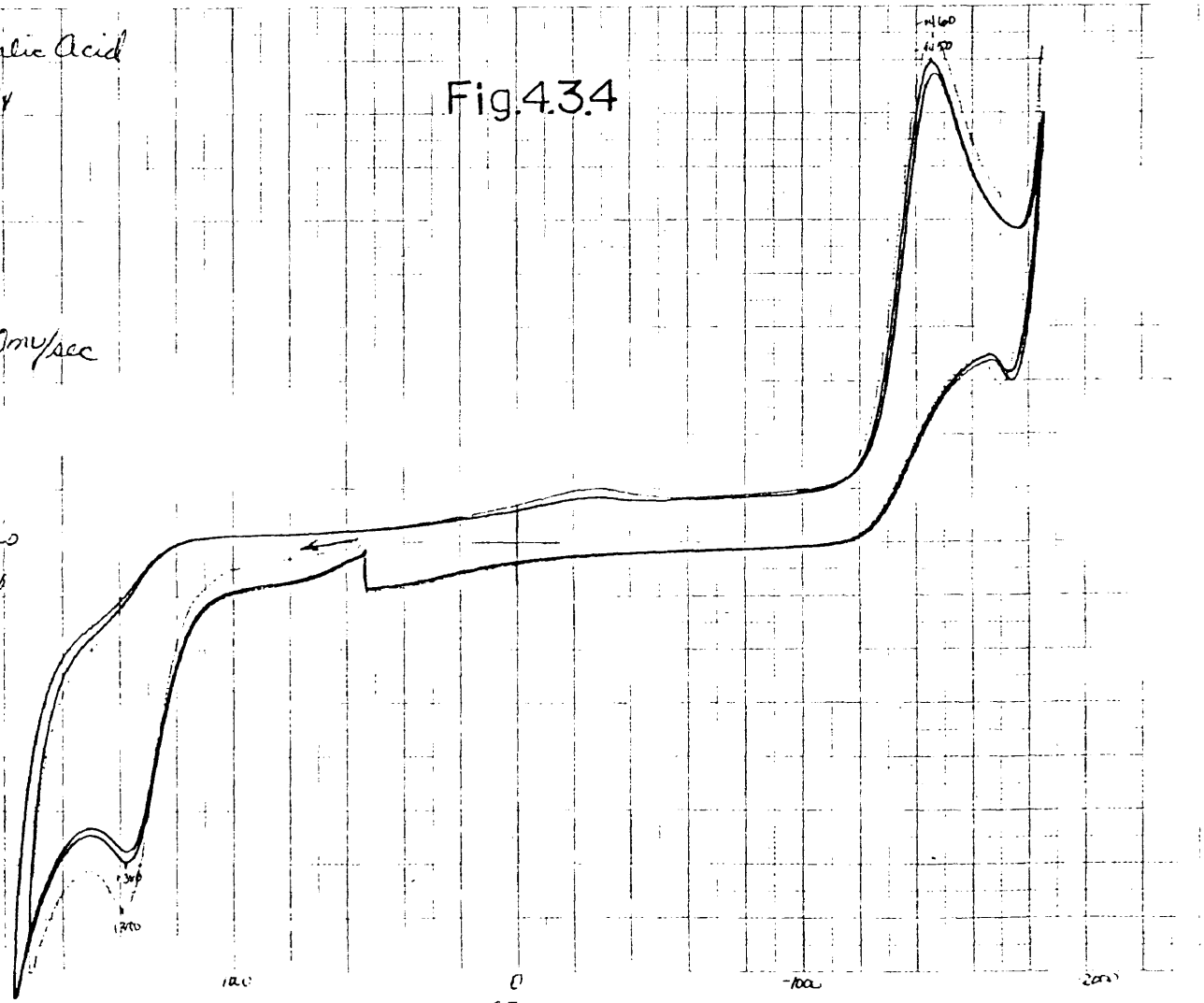
X = 200mv/cm

Y = 10uA/cm

Scan rate = 100mv/sec

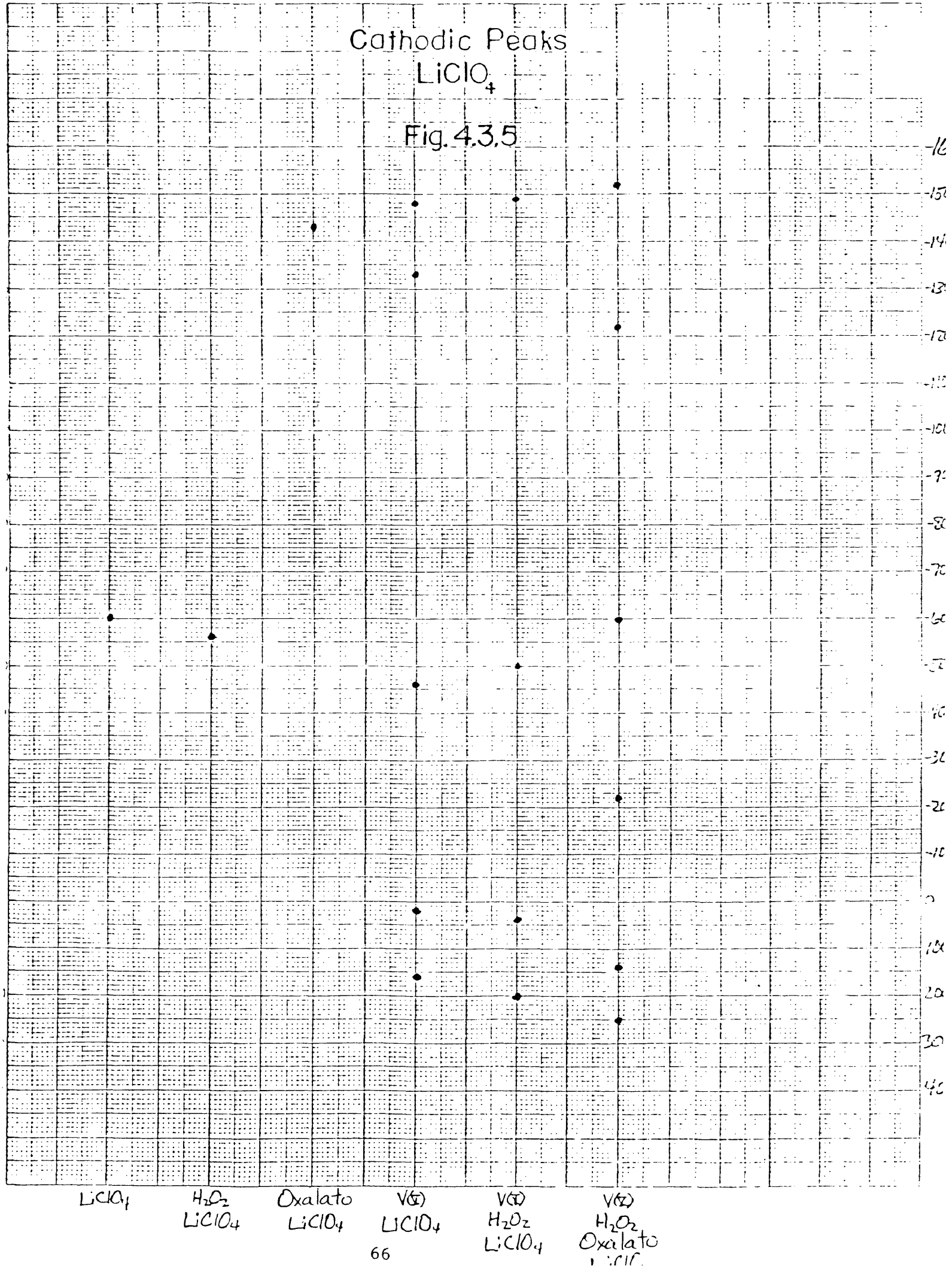
Blank $LiClO_4$ was run on Citric Acid scan.

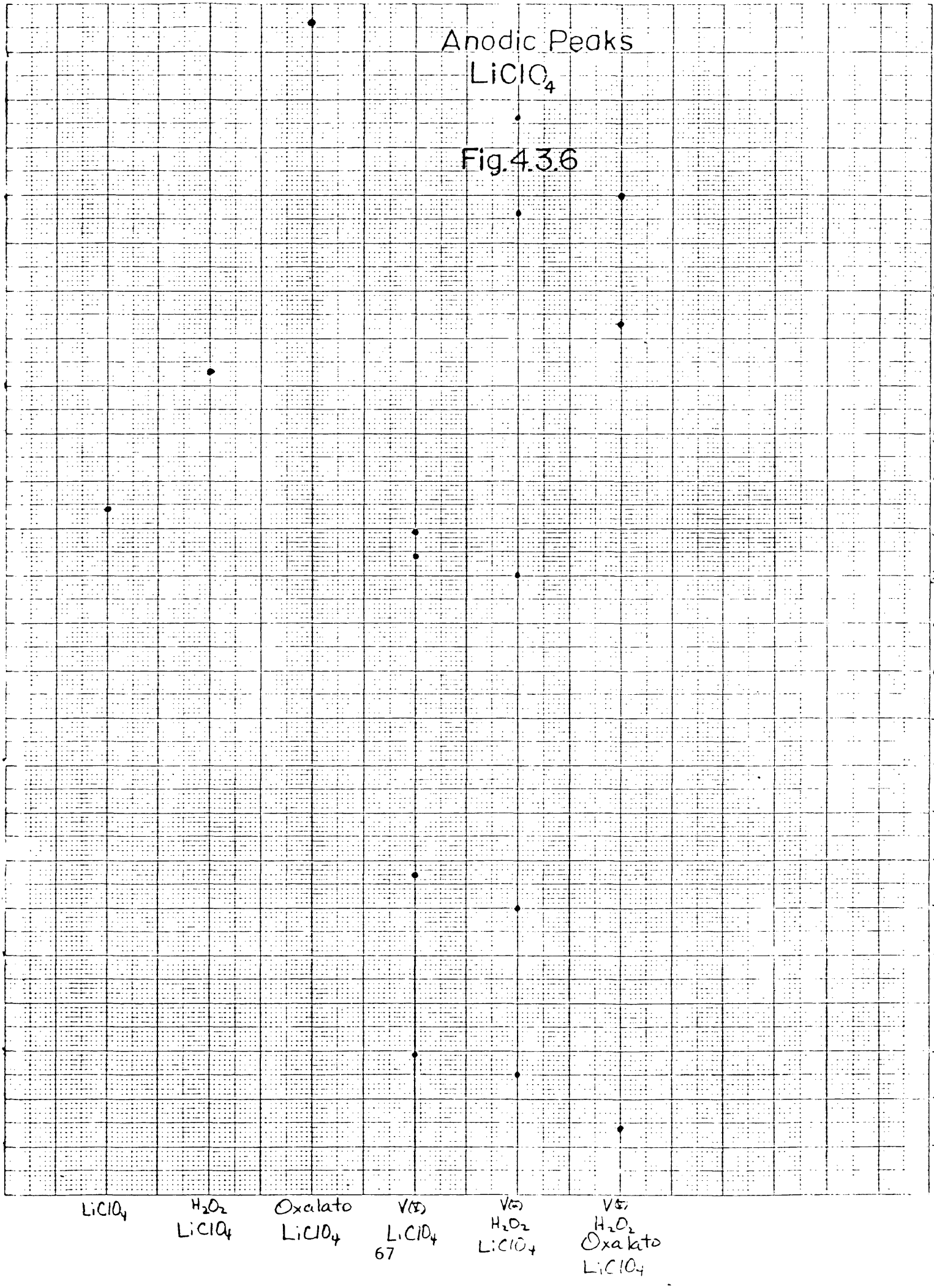
Fig. 4.3.4

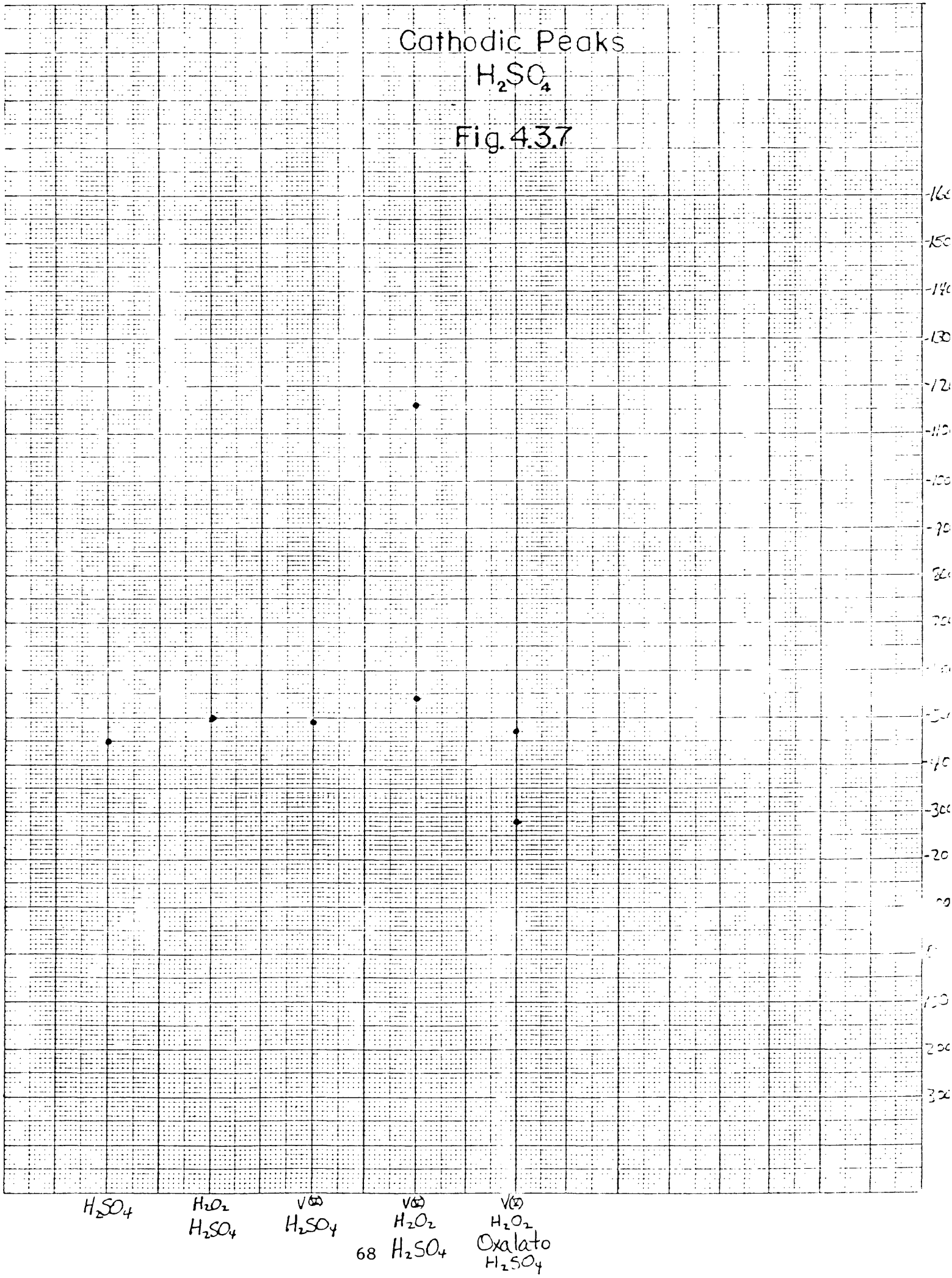


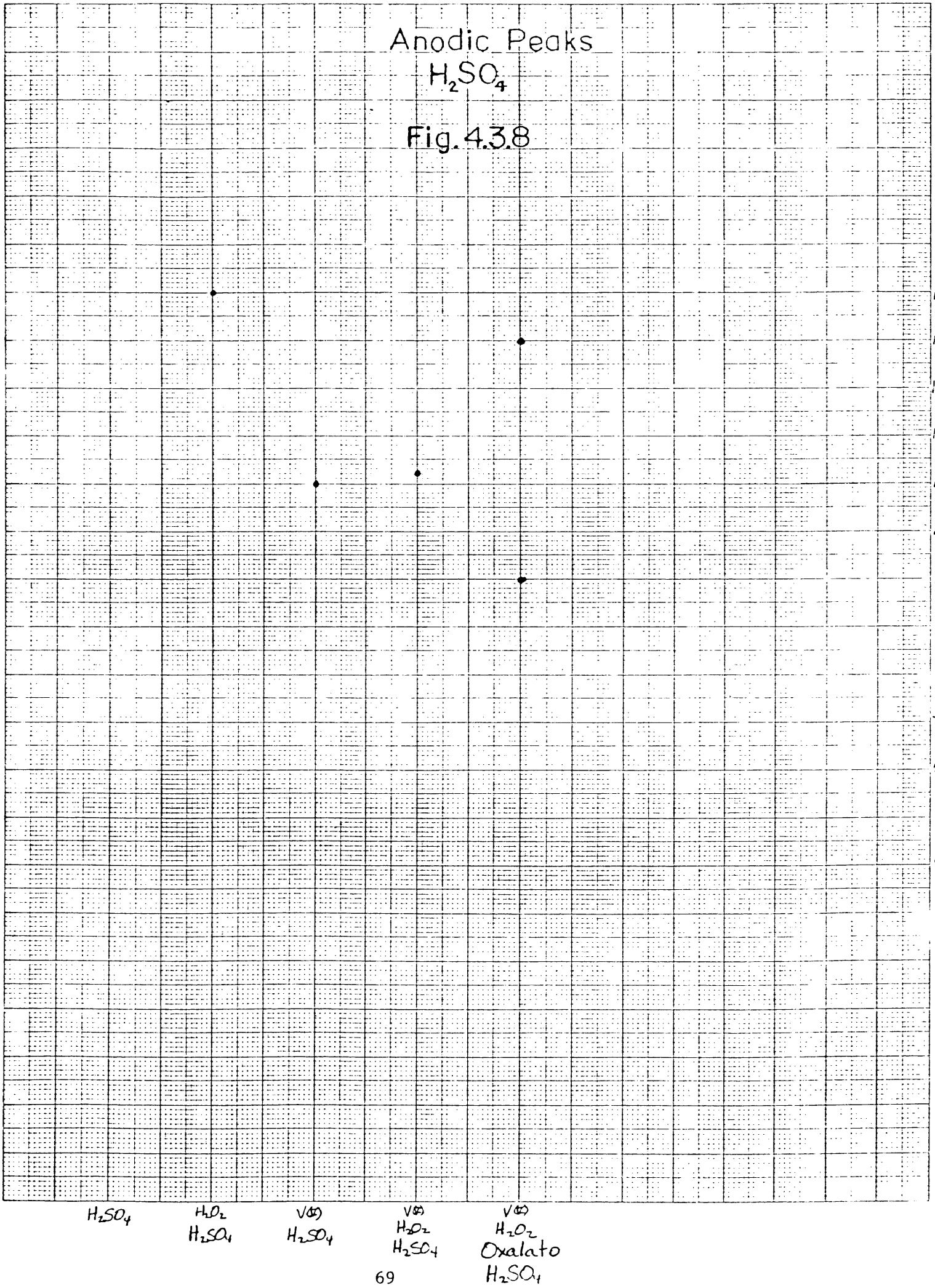
DJM p.129

5-20-80


Cathodic Peaks
$LiClO_4$
Fig. 4.3.5
$LiClO_4$
H_2O_2 $LiClO_4$
Oxalato $LiClO_4$
V(I) $LiClO_4$
V(I) H_2O_2 $LiClO_4$
V(I) H_2O_2 Oxalato $LiClO_4$


Anodic Peaks
$LiClO_4$
Fig. 4.3.6
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
-300
-400
-500
-600
-700
-800
$LiClO_4$
H_2O_2 $LiClO_4$
Oxalato $LiClO_4$
V(V) $LiClO_4$
V(V) H_2O_2 $LiClO_4$
V(V) H_2O_2 Oxalato $LiClO_4$


Cathodic Peaks
H_2SO_4
Fig. 4.3.7
H_2SO_4
H_2O_2 H_2SO_4
V(x) H_2SO_4
V(x) H_2O_2 H_2SO_4
V(x) H_2O_2 Oxalato H_2SO_4


Anodic Peaks
H_2SO_4
Fig. 4.3.8
16
15
14
13
12
11
10
9
8
7
6
5
4
H_2SO_4
H_2O_2 H_2SO_4
V(V) H_2SO_4
V(V) H_2O_2 H_2SO_4
V(V) H_2O_2 Oxalato H_2SO_4

4.4 PEROXO MALATO VANADATES

The oxoperoxomalato vanadates of the formula Na[$VO(O_2)$ malato][34] are new compounds and their structures are not known. In aqueous solution, they most likely rearrange. The electroactive species in the range +1.3 to -1.8V include V(V)/V(IV) and possibly V(IV/III) species as well as the malato ion since voltammograms of these solutions show peaks in this range.

Figures 4.4.1 and 4.4.2 show cyclic voltammograms of aqueous solutions of Na[$VO(O_2)$malato] and Cs[$VO(O_2)$malato] ($\sim x10^{-3}$M) in 0.2M $LiClO_4$ respectively. Three cycles are shown (curves 1, 2 and 3) and the starting potentials were approximately 500mV. The initial scan was cathodic.

To compare the electrochemical behavior of these compounds in aqueous solution with the electrochemistry of vanadium(V) in analogous systems, voltammograms shown in figures 4.1.1 through 4.1.8 and 4.4.3 through 4.4.8 were taken.

From the cyclic voltammograms of the various systems, the plots of the peak potentials, and the potentiometric titrations, the following observations are made:

1) On comparing the two malato compounds (fig. 4.4.1 and 4.4.2) in 0.2M $LiClO_4$ and pH≈3.0, one sees a significant difference in appearance of the voltammograms. However, on comparing the voltammogram of the cesium salt with the voltammogram of the month old sodium salt (fig. 4.4.3), one sees many similarities. This suggests that these compounds decompose with time and that the cesium salt probably decomposed before the voltammogram was run.

2) In 0.2M $LiClO_4$, the peak potentials of the compounds differ considerably from the peak potentials of the mixture of component solutions. This implies that under these conditions and time frame, the reactive species formed upon dissolution of the compounds are not the same as those formed by mixing the component solutions.

3) In 0.2M H_2SO_4, the voltammograms of the two compounds and the mixture of component solutions appear to be very similar. This indicates that the compounds under these conditions and time frame form the same electroactive species as does the mixture of components.

4) On comparing the shifts of the vanadium(V/IV) peaks at approximately 50 and 200mV one sees

a general trend toward more positive values for the series of vanadium, vanadium and peroxide, then vanadium, peroxide and malic acid (see fig. 4.4.9). However, these peaks are not present on the voltammograms of the compounds. These results show that the vanadium peaks are significantly affected by the presence of ligands and the degree of bonding to the ligand.

5) The potentiometric titration information shows good agreement between the stoichiometry and the reproducibility for the ammonium, potassium and cesium salts. The titration curve and characteristic potentials for the compounds match closely to the mixture of components in acid solutions.

Fig.4.4.1

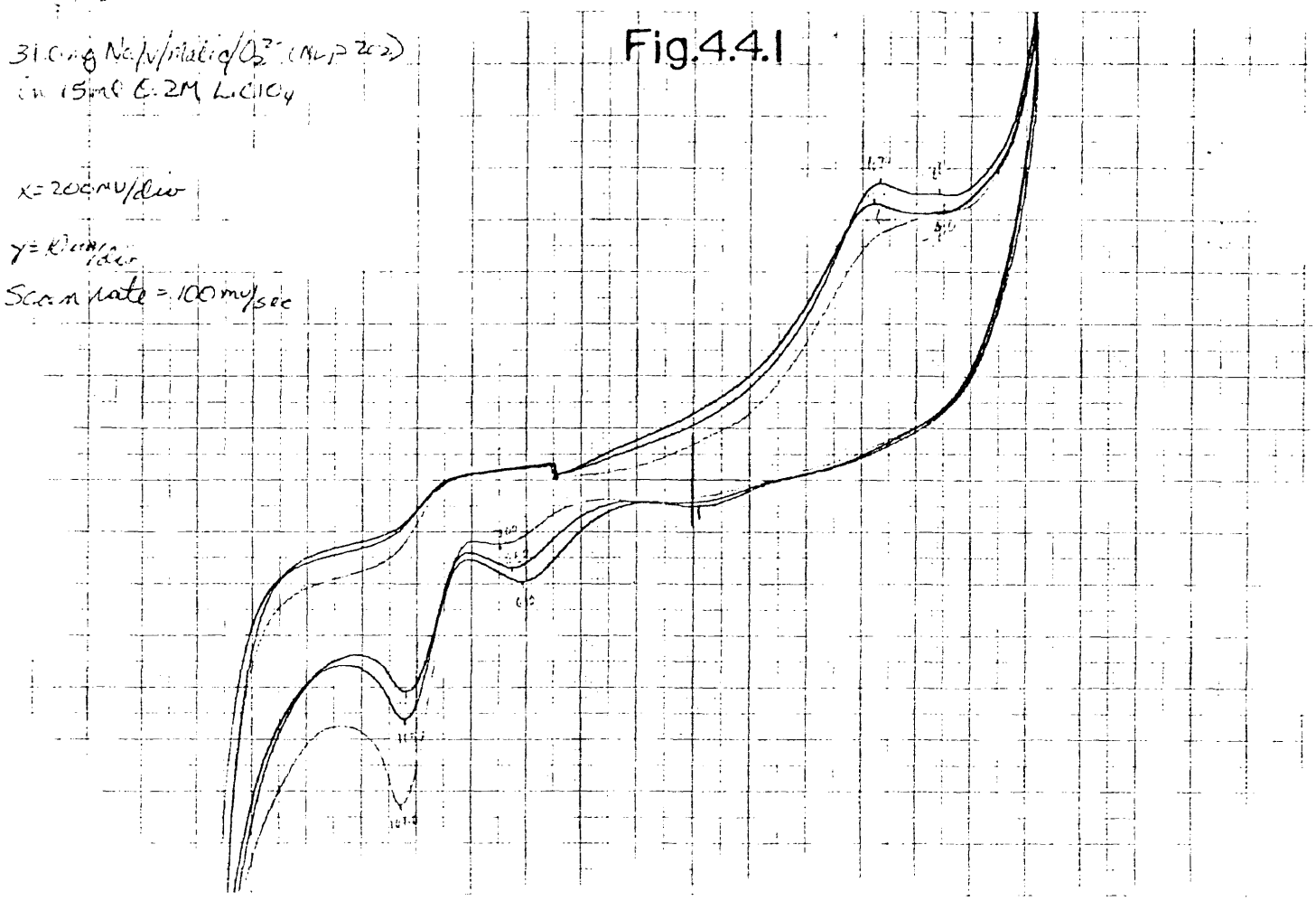
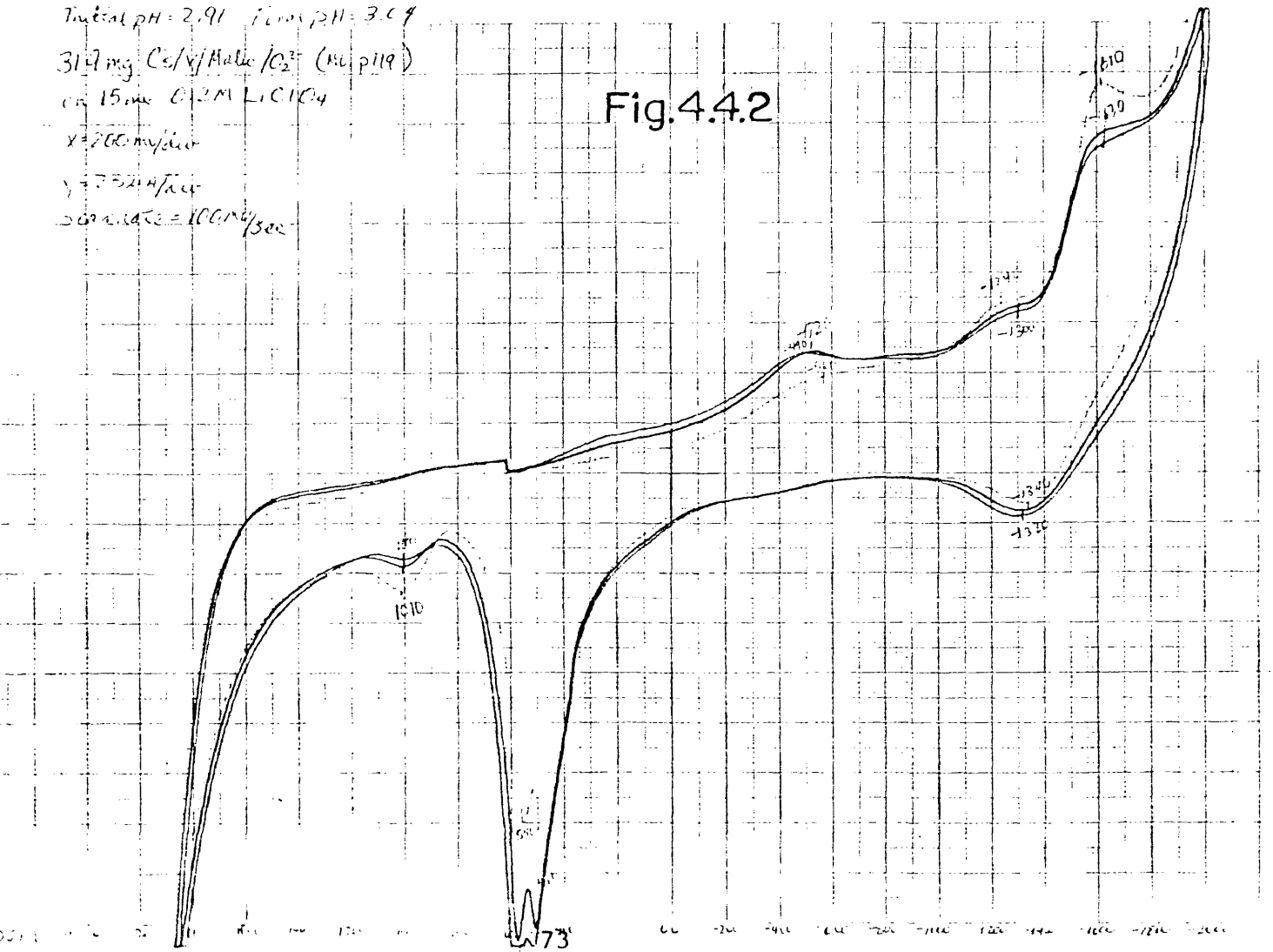


Fig.4.4.2



31.7mg Na/V/Malic/O_2^{2-} (ML p.202)

in 15 mL 0.2M $LiClO_4$.

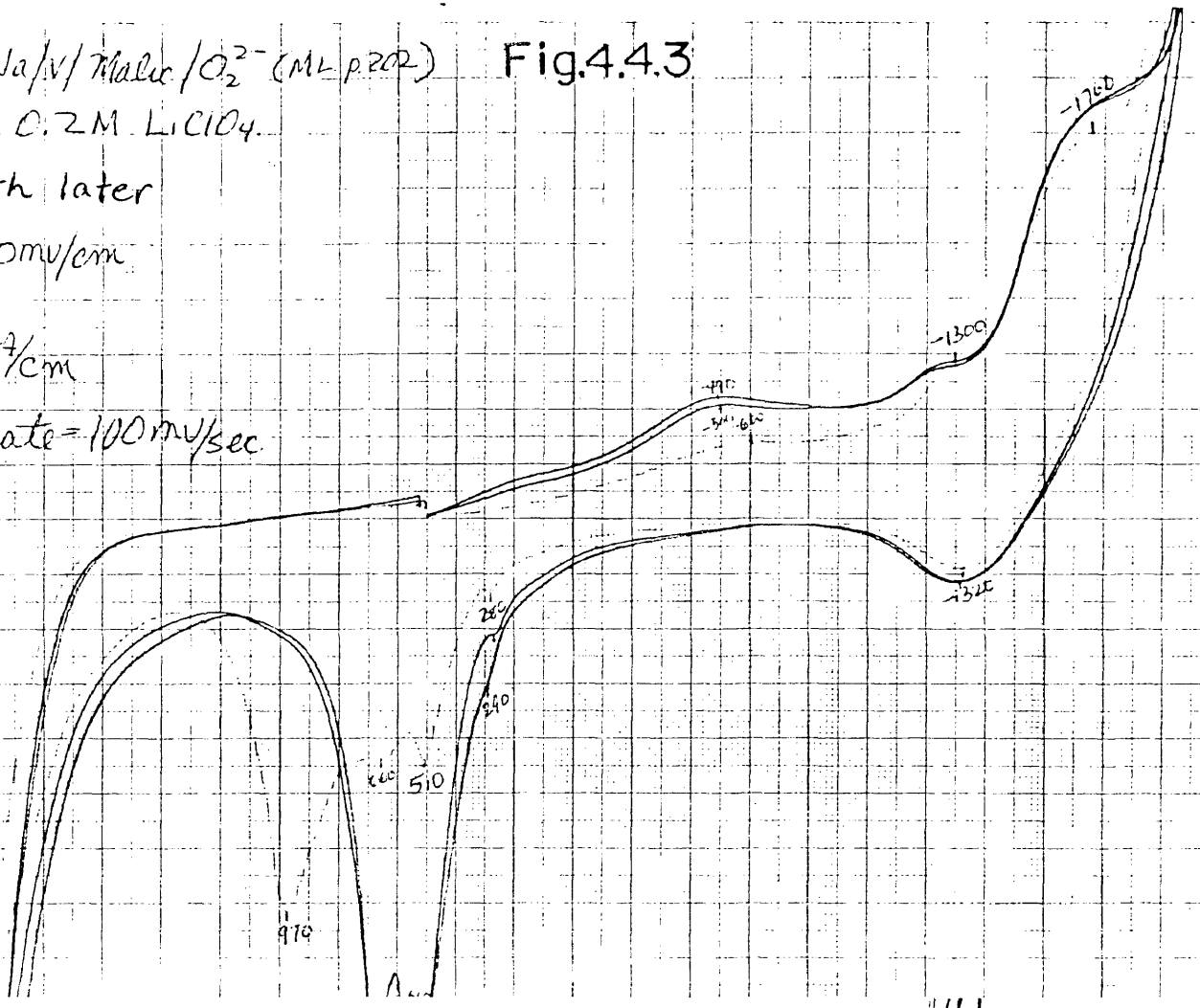
1 month later

X = 200mV/cm

Y = 25uA/cm

Scan rate = 100mV/sec

Fig.4.4.3



30.2mg Na/V/malic/O_2^{2-}

in 15mL 0.2M $LiClO_4$

X: 200 mV/div

Y: 25 mA/div

Scan rate: 100 mV/sec

Fig.4.4.4

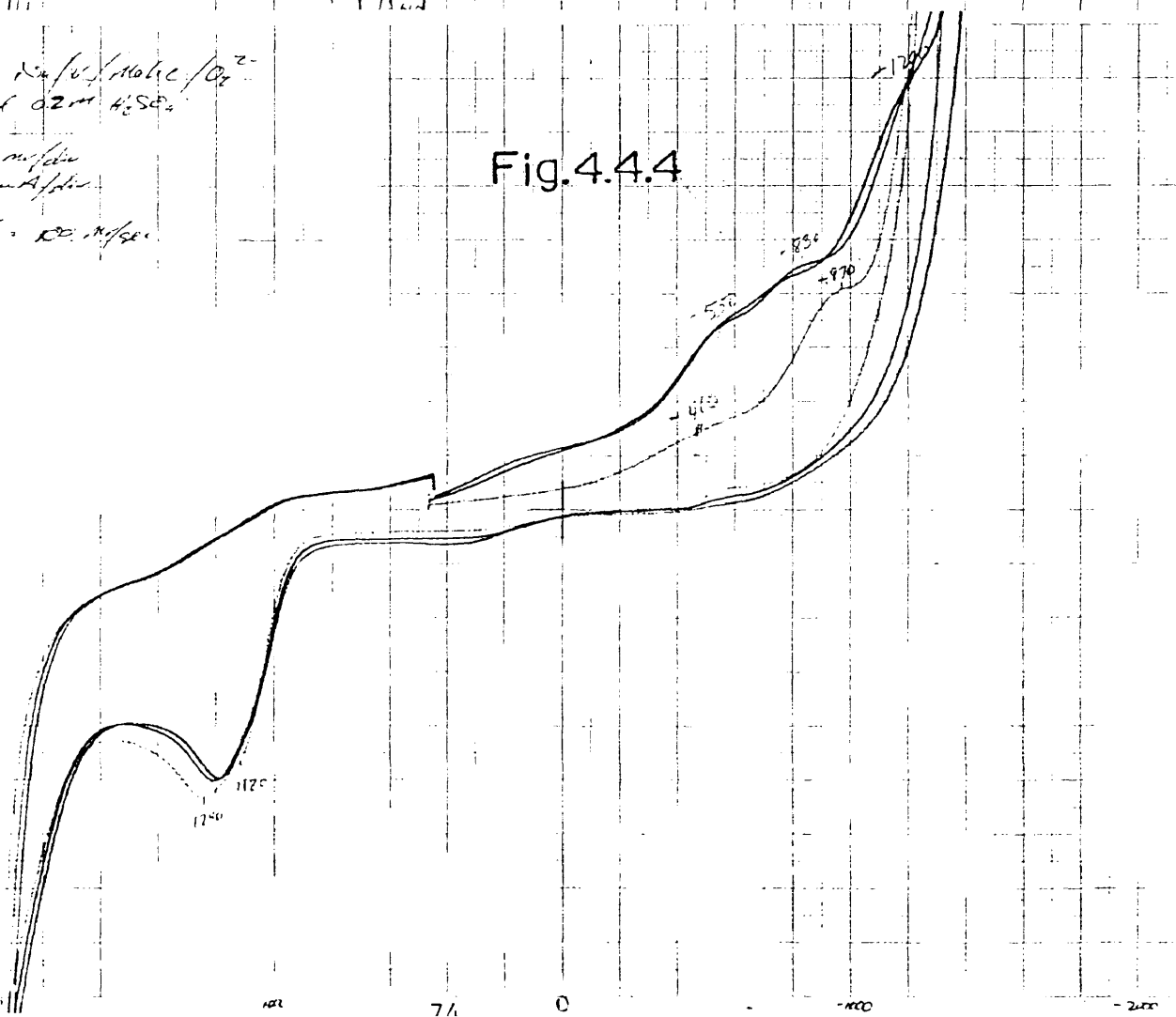
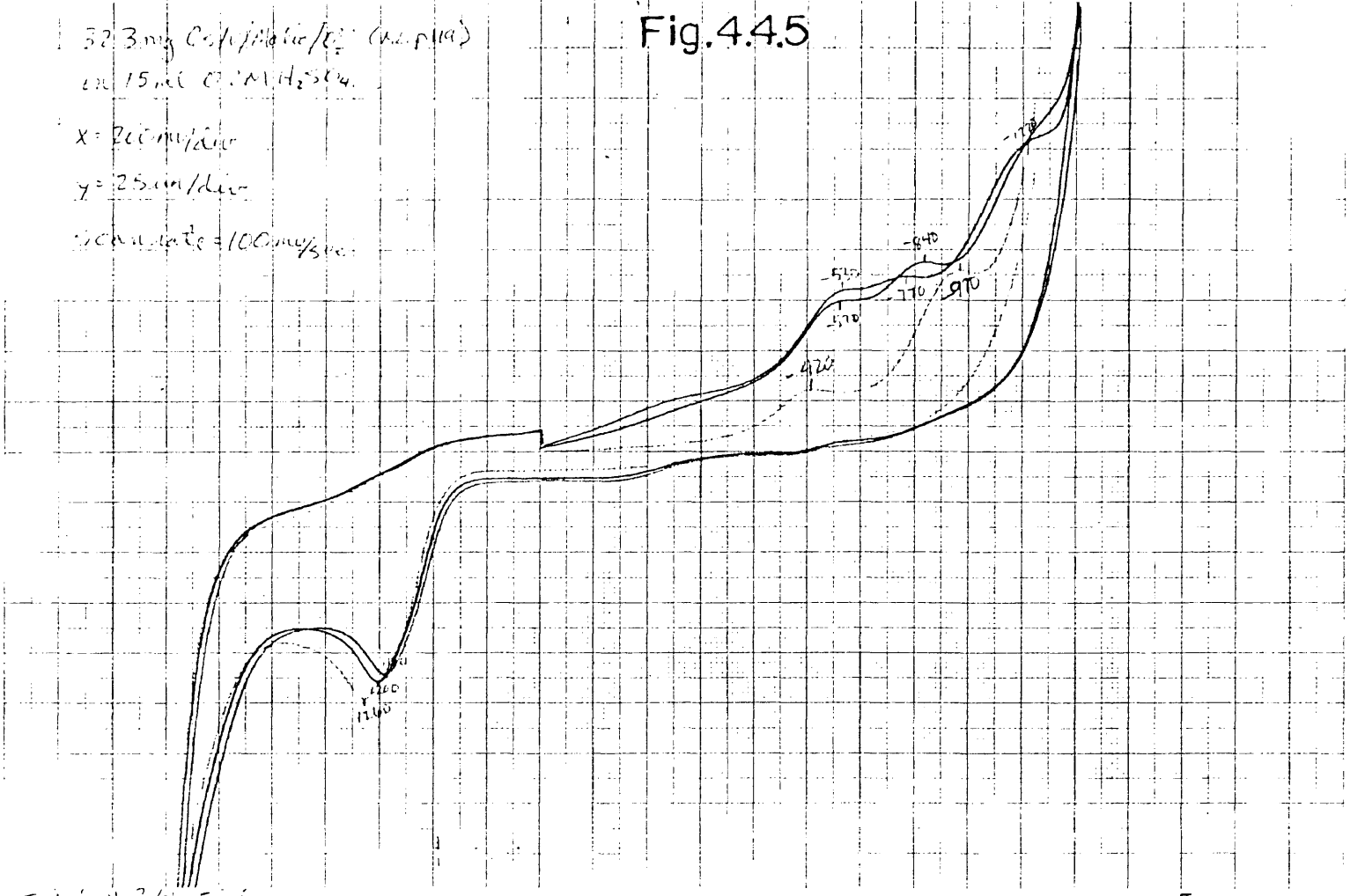
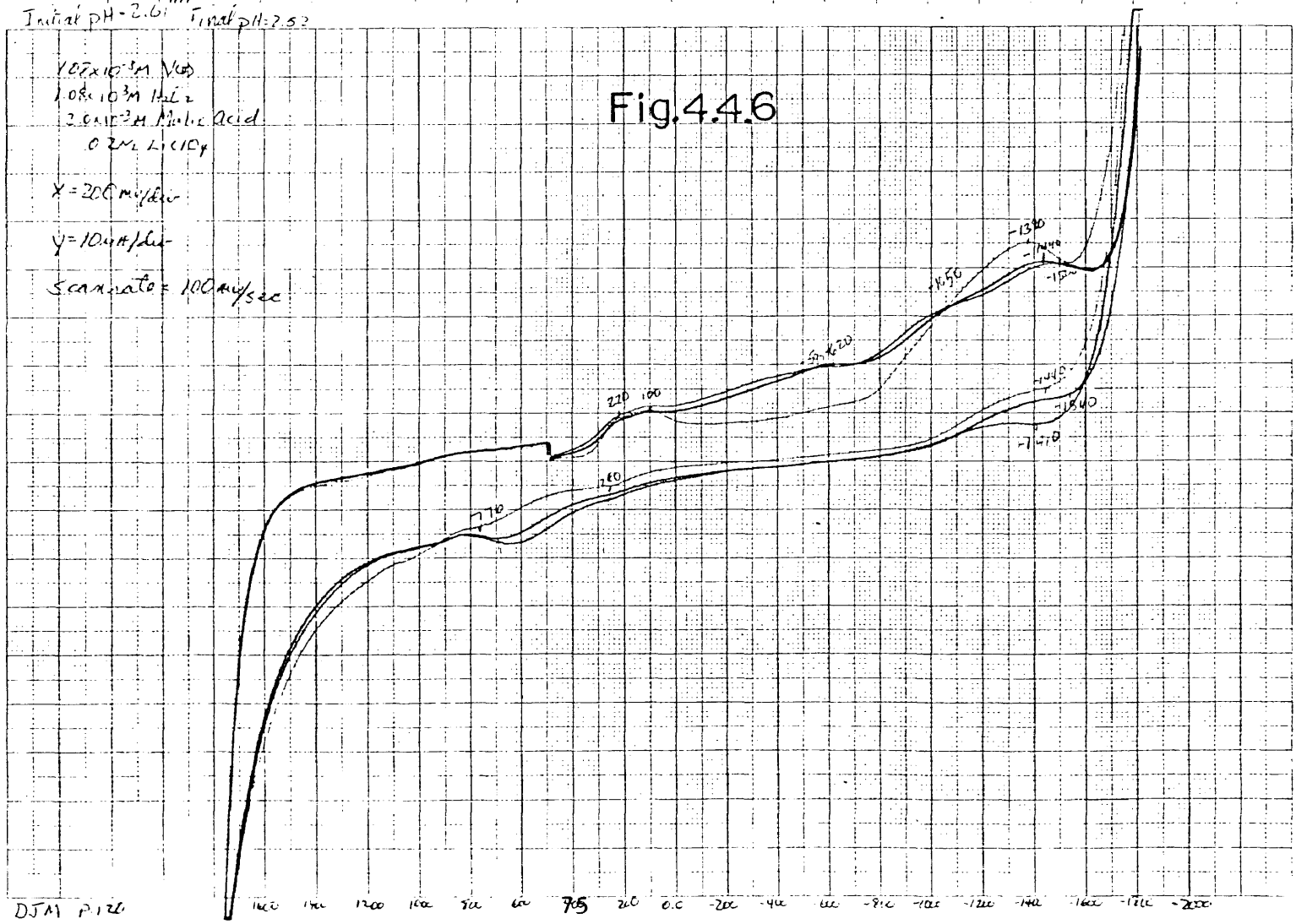


Fig.4.4.5



Initial pH - 2.61 Final pH: 2.53

Fig.4.4.6



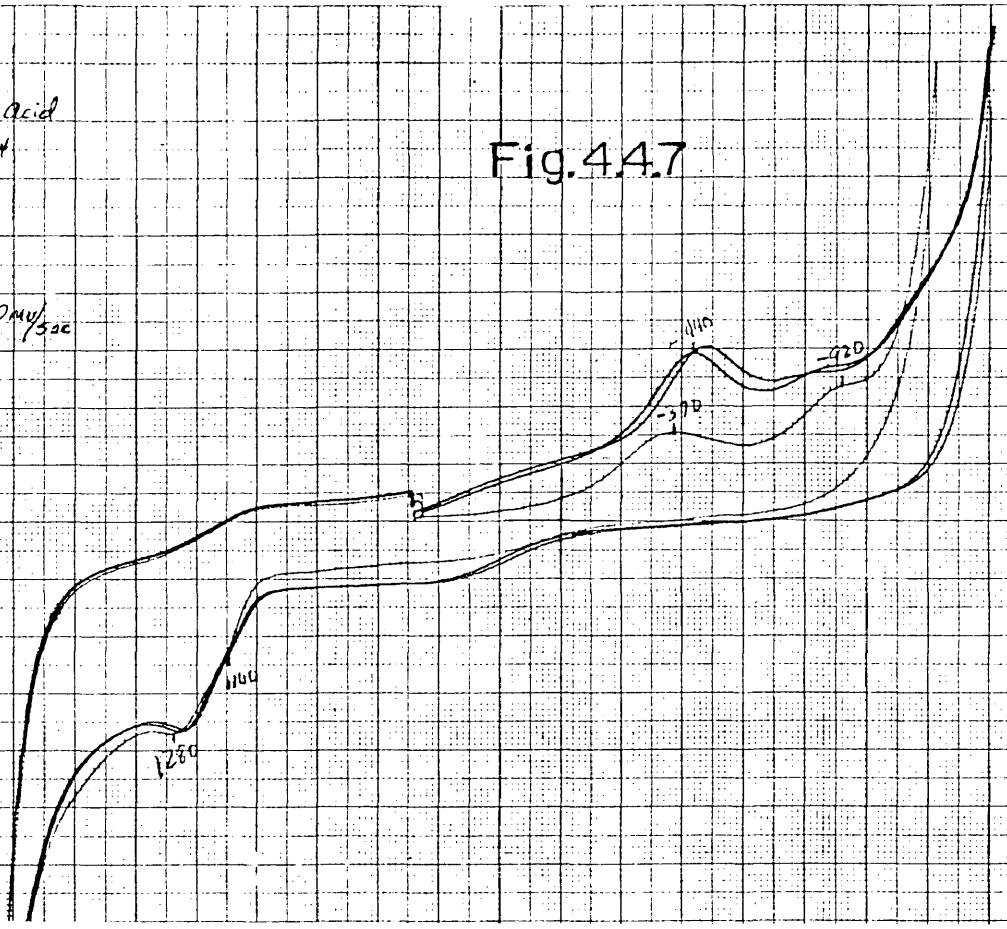
1.08×10^{-3}M VO
1.8×10^{-3}M H_2O_2
2.4×10^{-3}M Malic Acid
0.2M H_2SO_4

X = 200mv/div

Y = 10uA/div

Scan rate = 100mv/sec

Fig.4.4.7



PH=3.02

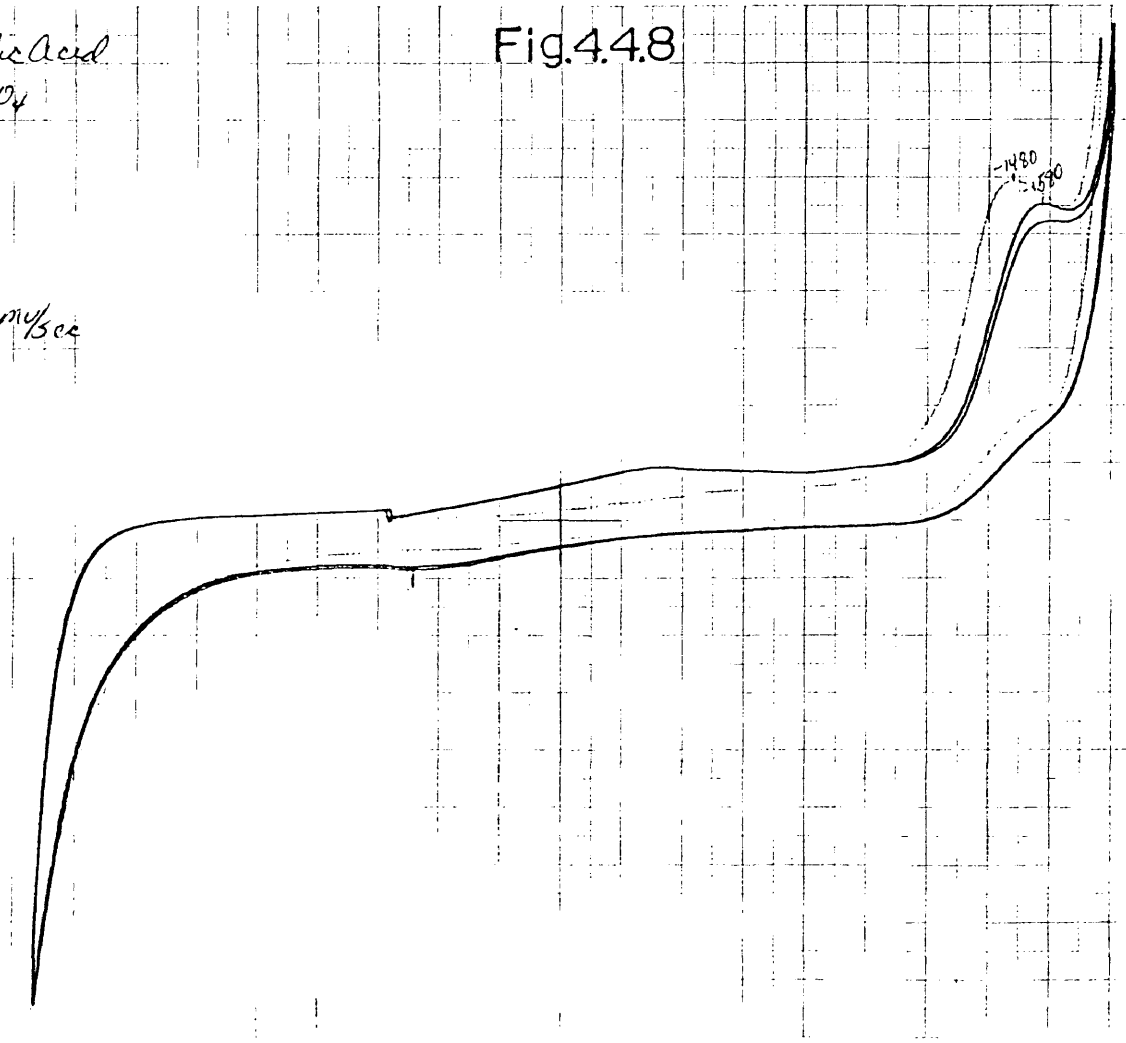
2.0×10^{-3}M Malic Acid
0.2M $LiClO_4$

X = 200mv/cm

Y = 10uA/cm

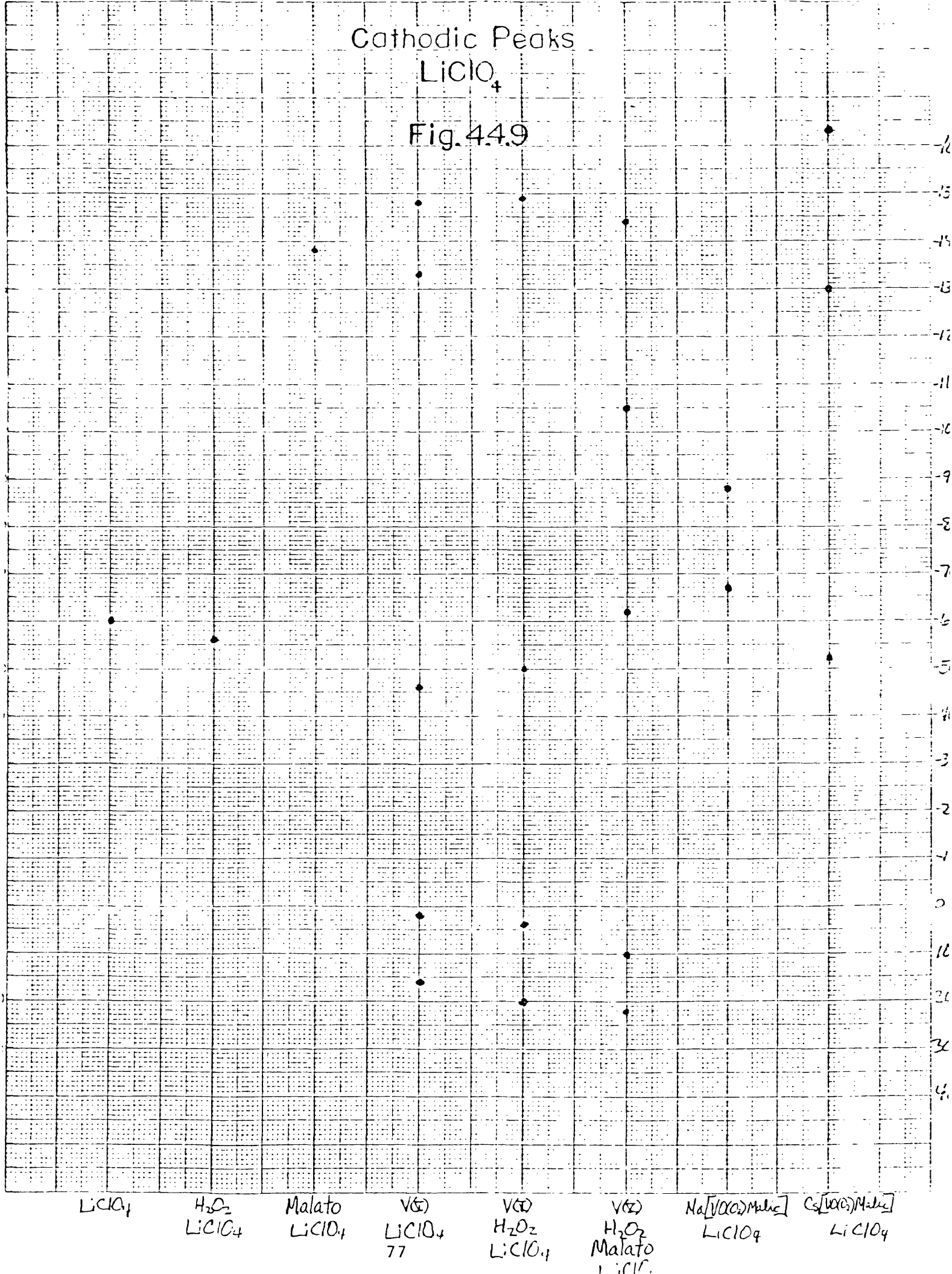
Scan rate = 100mv/sec

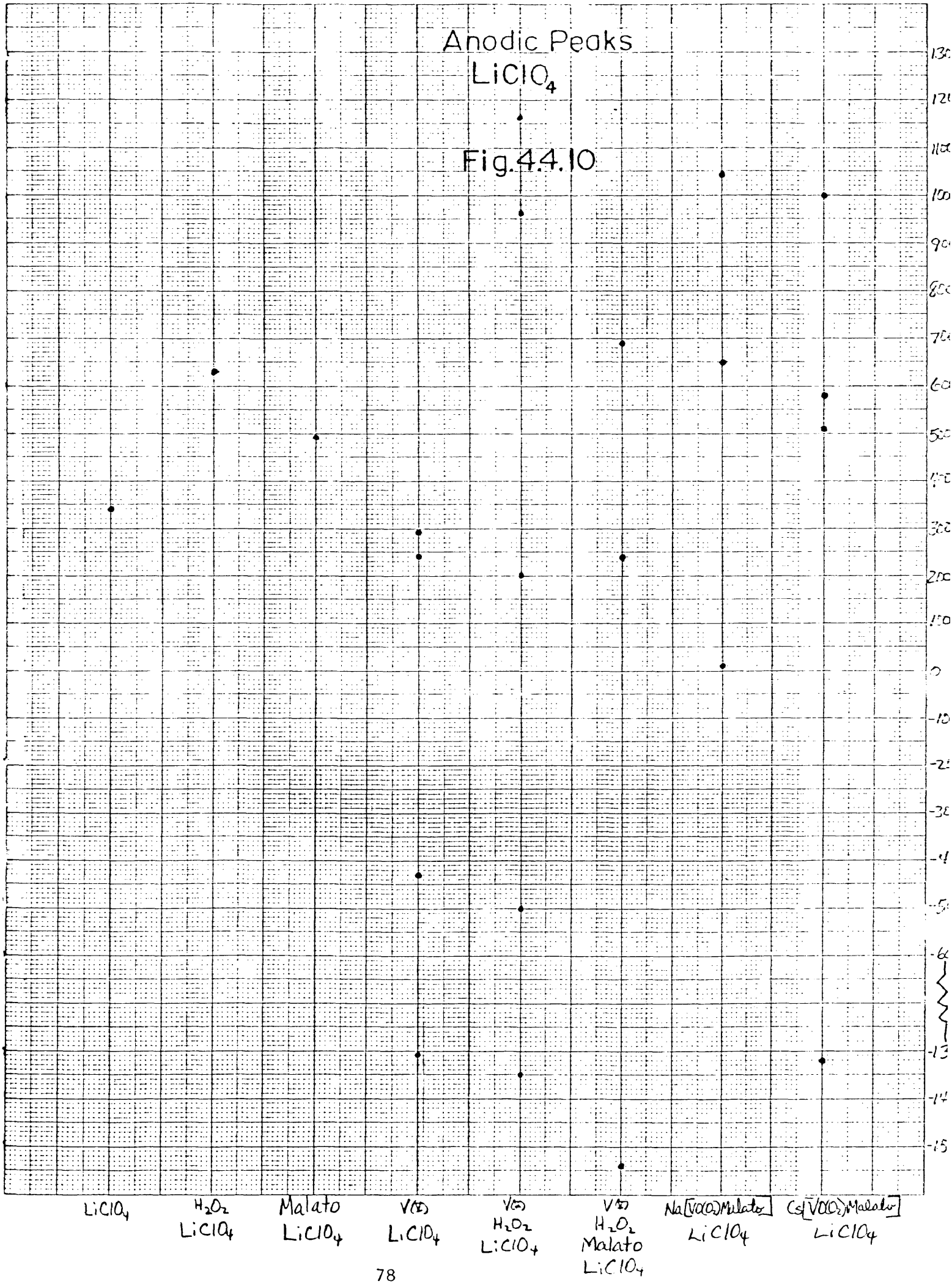
Fig.4.4.8

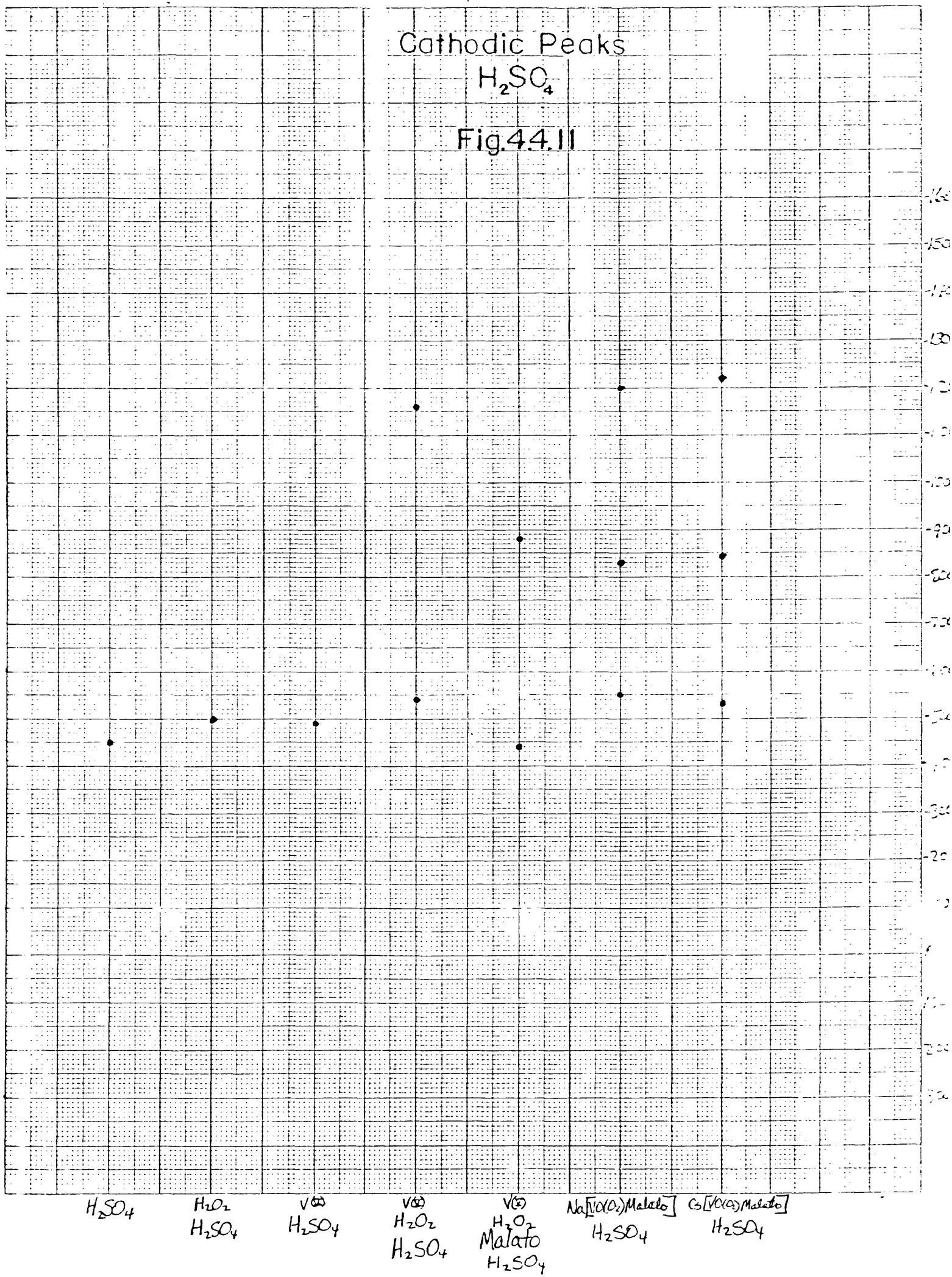


DJM 5-24-84

P.34

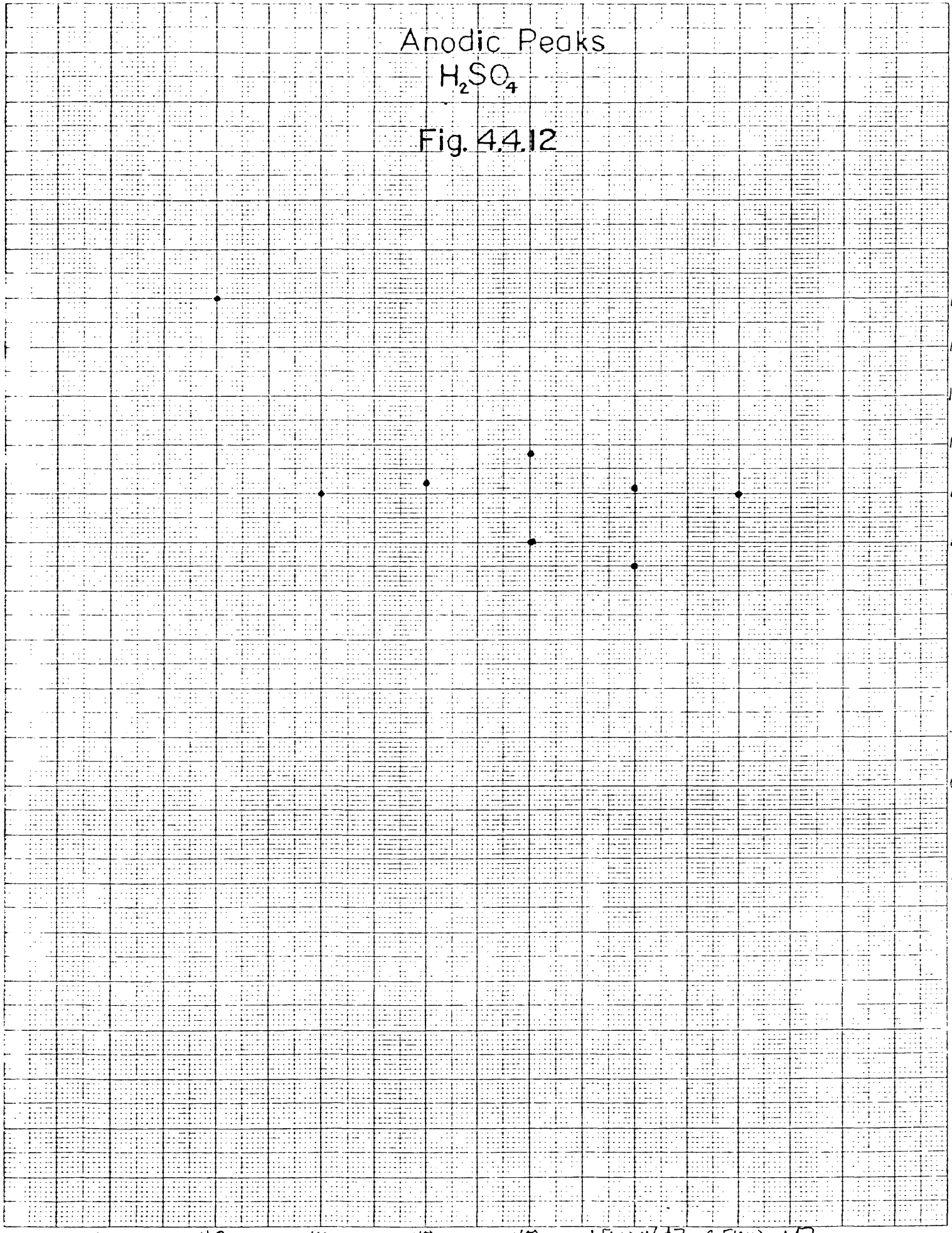

Cathodic Peaks
$LiClO_4$
Fig. 4.4.9
$LiClO_4$
H_2O_2 $LiClO_4$
Malato $LiClO_4$
V(V) $LiClO_4$
V(V) H_2O_2 $LiClO_4$
V(V) H_2O_2 Malato $LiClO_4$
$Na[VO(O_2)Malic]$ $LiClO_4$
$Cs[VO(O_2)Malic]$ $LiClO_4$


Anodic Peaks
LiClO4
Fig.44.10
LiClO4
H2O2 LiClO4
Malato LiClO4
V(V) LiClO4
V(V) H2O2 LiClO4
V(V) H2O2 Malato LiClO4
Na[VO(O2)Malato] LiClO4
Cs[VO(O2)Malato] LiClO4


Cathodic Peaks
H_2SO_4
Fig.4.4.11
H_2SO_4
H_2O_2 H_2SO_4
V(IV) H_2SO_4
V(IV) H_2O_2 H_2SO_4
V(IV) H_2O_2 Malato H_2SO_4
Na[V(IV)(O2)Malato] H_2SO_4
Cs[V(IV)(O2)Malato] H_2SO_4

Anodic Peaks
H_2SO_4

Fig. 4.4.12



4.5 PEROXO CITRATO VANADATES

The oxoperoxocitrato vanadates of the formula K[VO(O_2) citrato]^{34} and Na[VO(O_2)citrato]^{34} are new compounds and their structures are known. In aqueous solution they most likely rearrange. The electroactive species in the range +1.2 to -1.7V may include V(V)/V(IV) and V(IV)/V(III) species as well as the citrate ion since voltammograms of these solutions show peaks in this range.

Figure 4.5.1 shows a cyclic voltammogram of an aqueous solution of K[VO(O_2)citrato] and fig. 4.5.2 shows Na[VO(O_2) citrato]. Both are (~x10^{-3}M) in 0.2M $LiClO_4$. Three cycles are shown for both and the initial starting potentials are approximately 500mV. The initial scans are cathodic.

To compare the electrochemical behavior of these compounds in aqueous solution with the electrochemistry of vanadium(V) in analogous systems, voltammograms shown in figures 4.5.3 through 4.5.7 were taken.

From the cyclic voltammograms of the various systems, the plots of the peak potentials, the following observations are made:

1) On comparing the voltammograms of the two compounds in 0.2M $LiClO_4$(pH = 2.85) one notices a considerable

difference in the number and position of peaks present. The most obvious difference is the additional anodic peaks that appear on successive cycles for the potassium salt. These additional peaks are an indication that chemical processes are occurring along with the electrochemical processes.

2) On comparing the voltammograms of the two compounds in 0.2M H_2SO_4 one also notices a considerable difference in the number and position of peaks present. the voltammogram of the potassium salt appears to be very similar to the mixture of peroxovanadates in the absence of a heteroligand (fig. 4.1.8). This is not true for the sodium salt.

This information suggests that the compound K[VO(O_2) citrato] may have decomposed before the voltammograms were taken.

3) In 0.2M $LiClO_4$ the peak potentials of the sodium salt (fig. 4.5.2) differs significantly from the peak potentials of the mixture of components (fig. 4.5.6). This is also the case for the compound in 0.2M H_2SO_4. This information implies that the electroactive species formed upon dissolution of the citrato compound are not the same as those

formed upon mixing of the components which implies some degree of stability of the citrato compound.

4) On comparing the voltammograms of the various systems, the following differences and shifts are observed. Vanadium (V/IV) peaks near 50 and 200mV show a trend toward more positive values when peroxide, then peroxide and citric acid is added to vanadium in 0.2M $LiClO_4$ (see fig. 4.5.8). However, this trend is not followed by the compounds. These results indicate that vanadium (V/IV) peaks are significantly effected by the presence and degree of association of the citrato ligand.

5) The potentiometric titrations have shown that near stoichiometric amounts of peroxo ions present in solution. The reproducibility of potentials at characteristic points is very good for the potassium and ammonium citrato compounds tested. The compounds displayed a similar behavior to that of the mixture of component in acid solutions.

30.6 mg K/V/Cd/O_2^{2-} (ML p192)

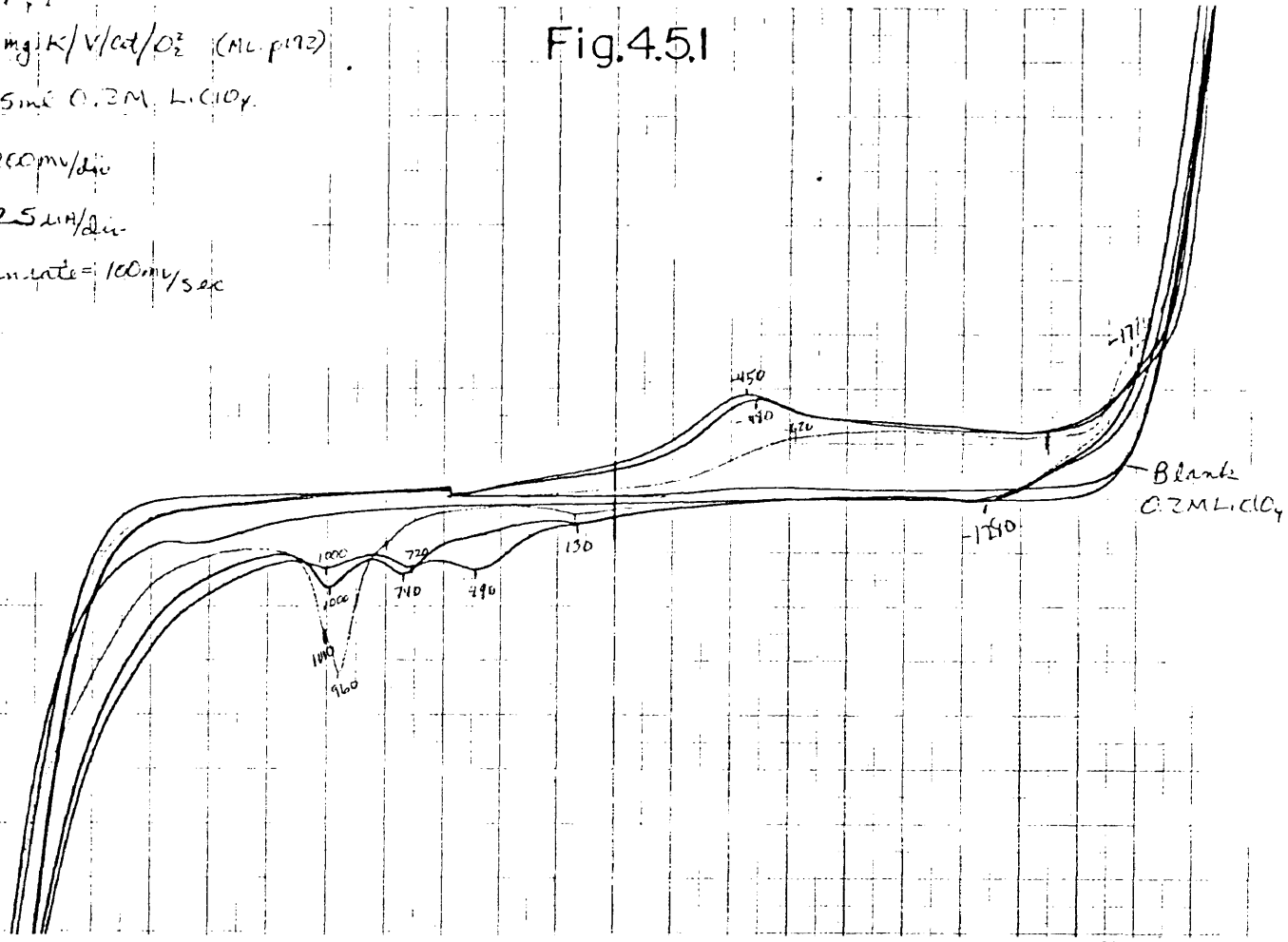
in 15 mL 0.2M $LiClO_4$

x = 200 mV/div

y = 2.5 μA/div

scan rate = 100 mV/sec

Fig. 4.5.1



pH 7.85

32.4 mg Hg/L/platinic acid/O_2^{2-}

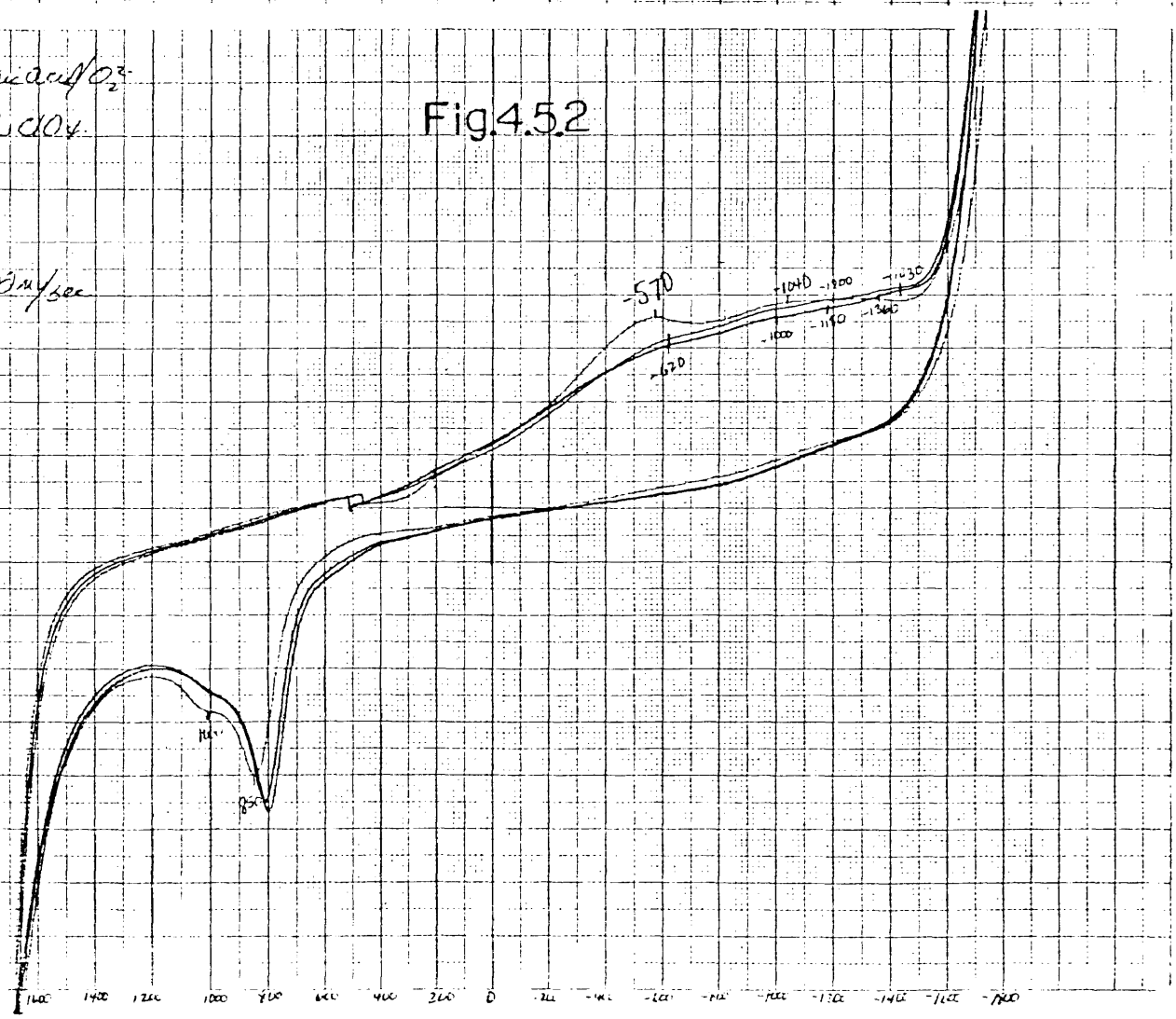
in 15 mL 0.2M $LiClO_4$

x = 200 mV/div

y = 1 μA/div

Scan rate = 100 mV/sec

Fig. 4.5.2



DJM p121
1-12-84

31.4 mg K/V/Cu/Cl_2^{2-} (ML P192)

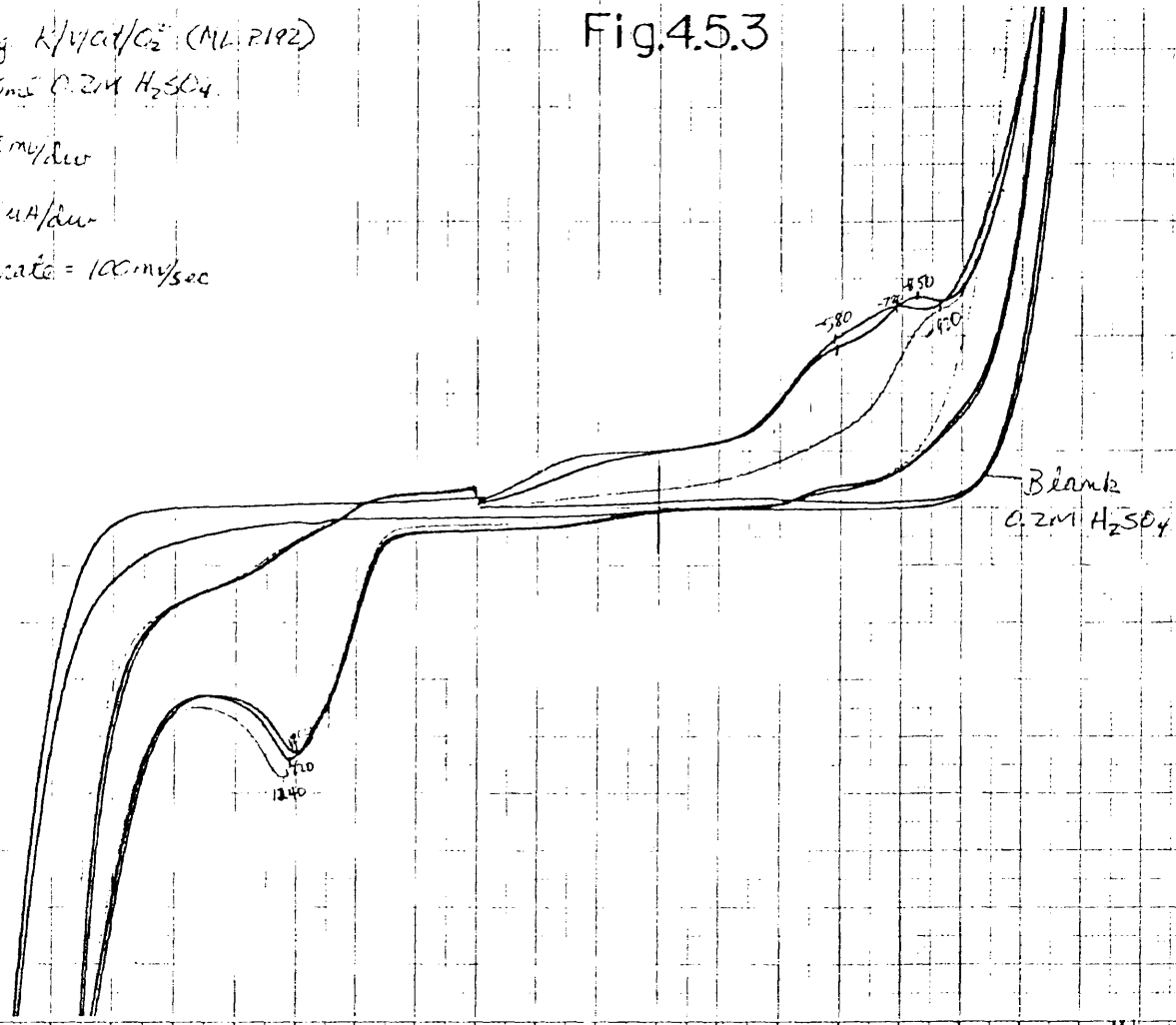
in 15 ml 0.2M H_2SO_4

x = 200 mv/div

y = 25 uA/div

scan rate = 100 mv/sec

Fig. 4.5.3



30.7 mg Nb/V/Cu/Cl_2^{2-} in

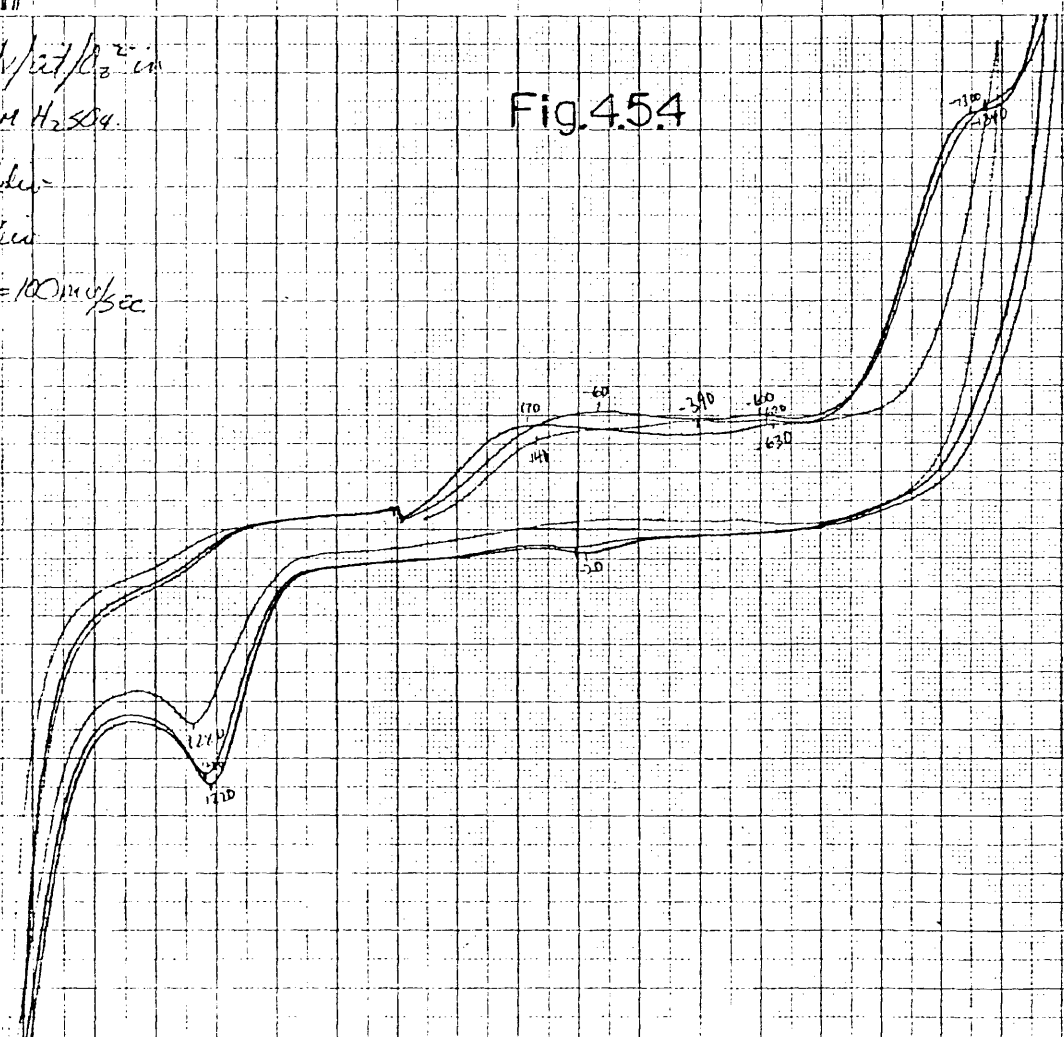
15 ml 0.2M H_2SO_4

X = 200 mv/div

Y = 25 uA/div

Scan rate = 100 mv/sec

Fig. 4.5.4



DJM p 121

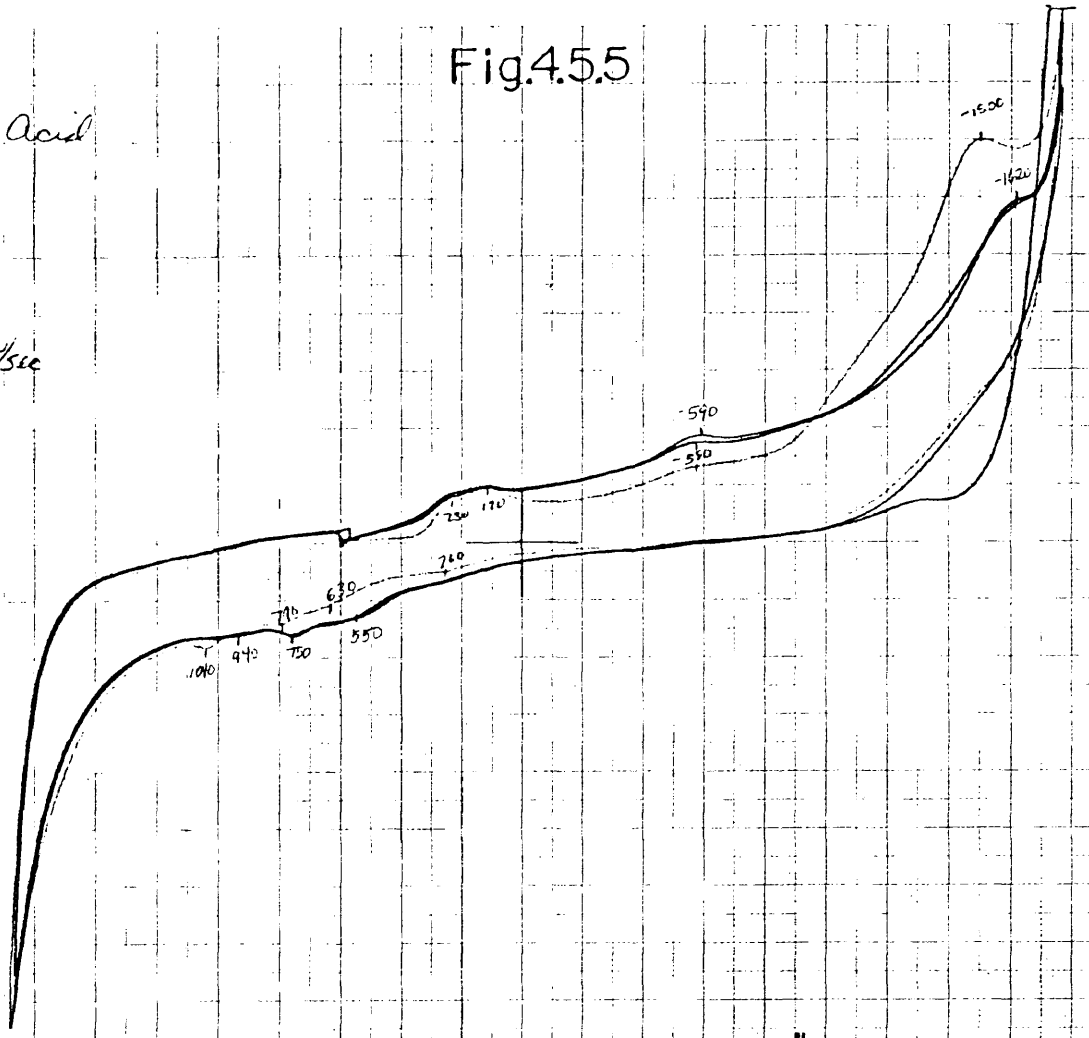
pH = 2.14
1.00×10^{-3}M V(IV)
1.08×10^{-3}M H_2O_2
2.0×10^{-3}M Citric Acid
0.2M $LiClO_4$

X = 200 mv/cm

y = 10 μA/cm

Scan rate = 100 mv/sec

Fig.4.5.5



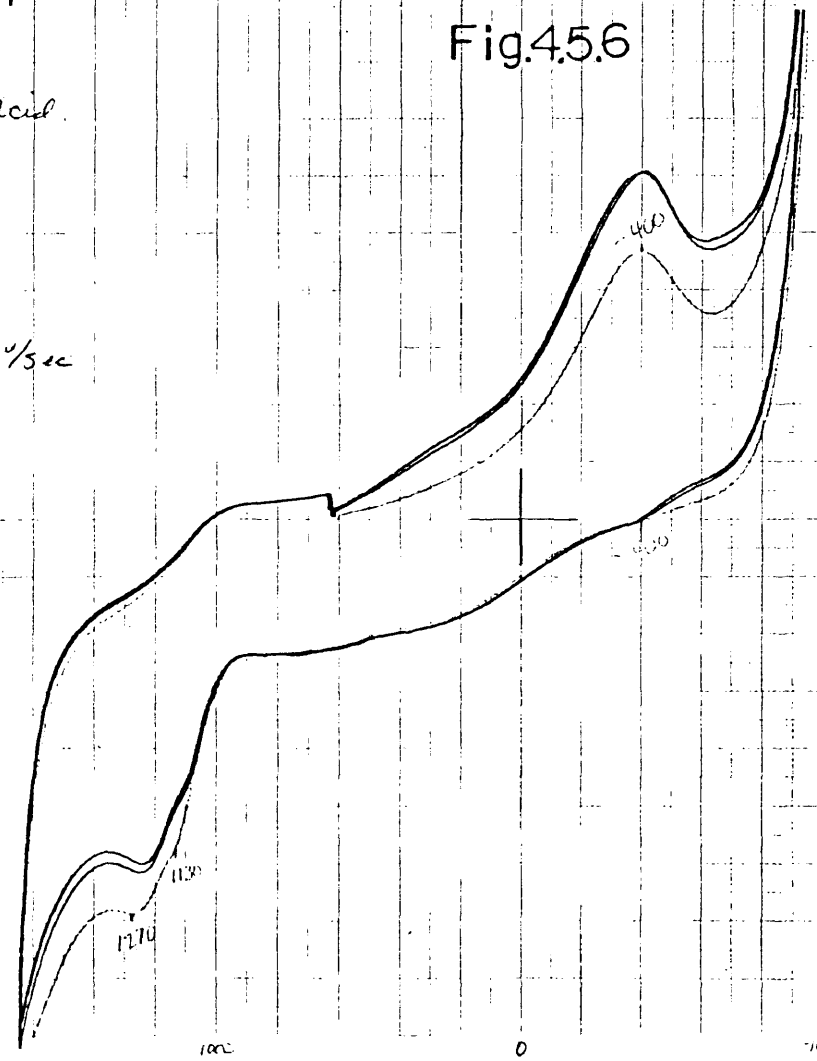
1.00×10^{-3}M V(IV)
1.08×10^{-3}M H_2O_2
2.0×10^{-3}M Citric Acid
0.2M H_2SO_4

X = 200 mv/cm

y = 5 μA/cm

Scan rate = 100 mv/sec

Fig.4.5.6



pH=2.90

2.0×10^{-3}M Citric Acid

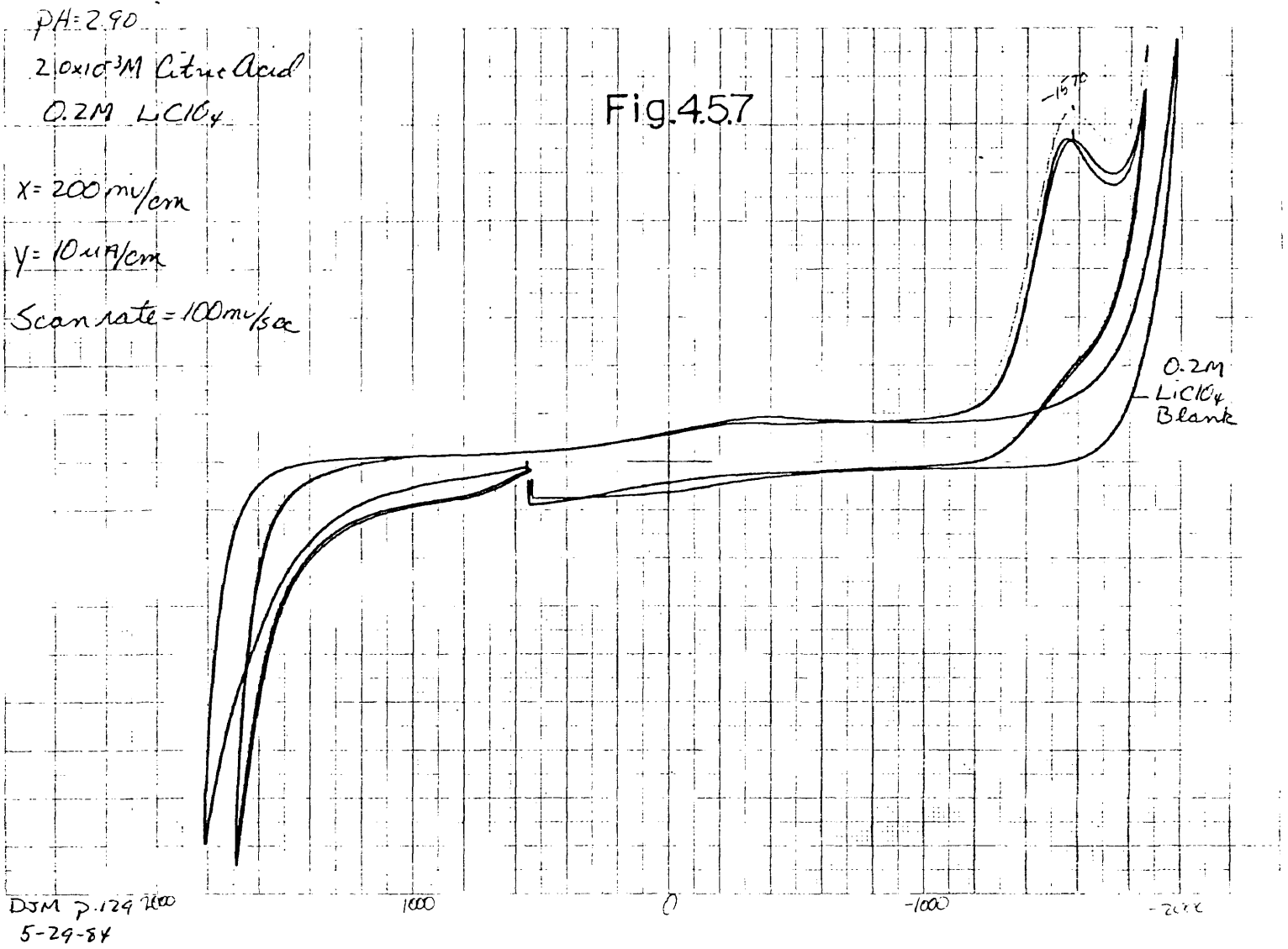
0.2M $LiClO_4$

X= 200 mv/cm

Y= 10 uA/cm

Scan rate = 100 mv/sec

Fig. 4.5.7

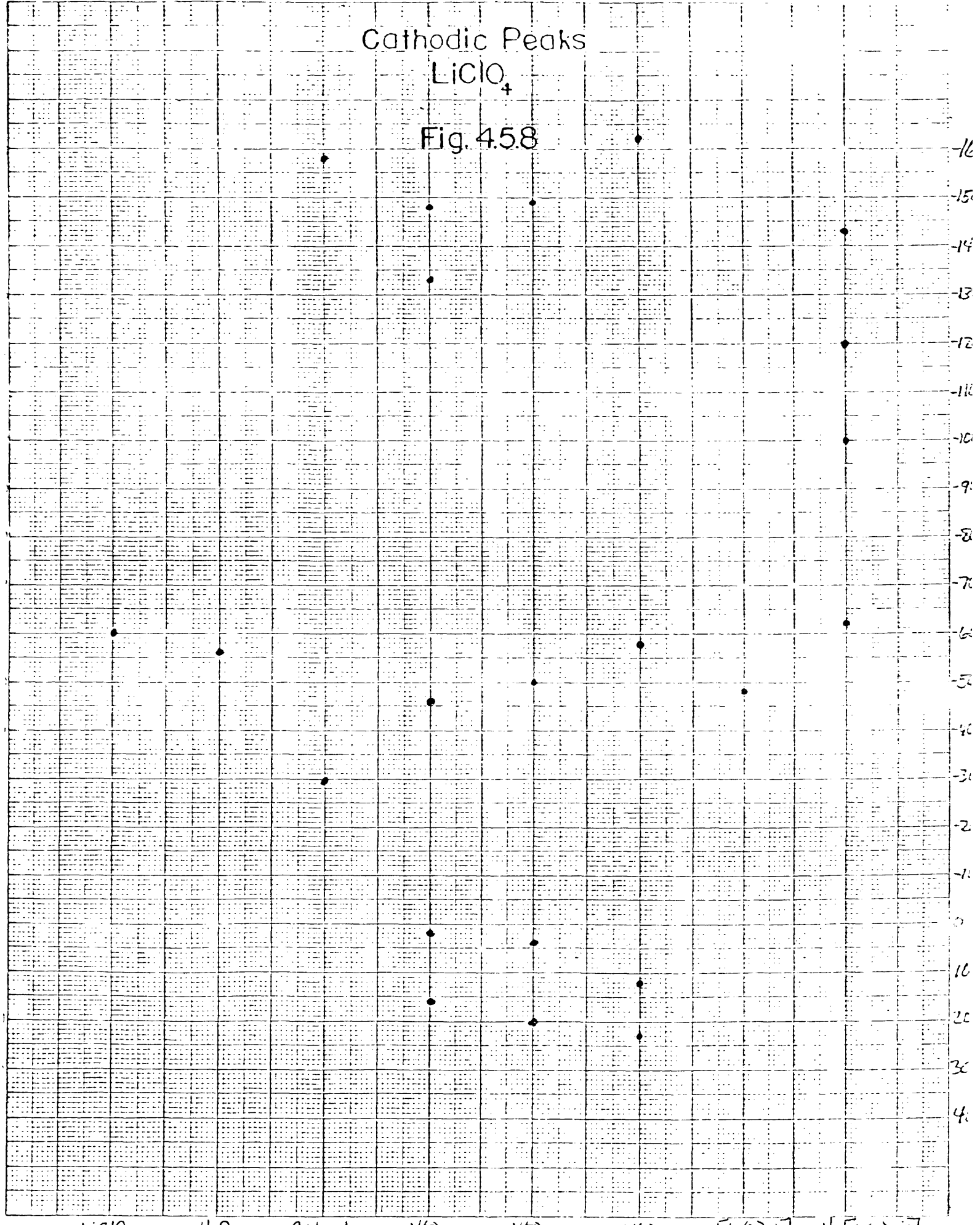


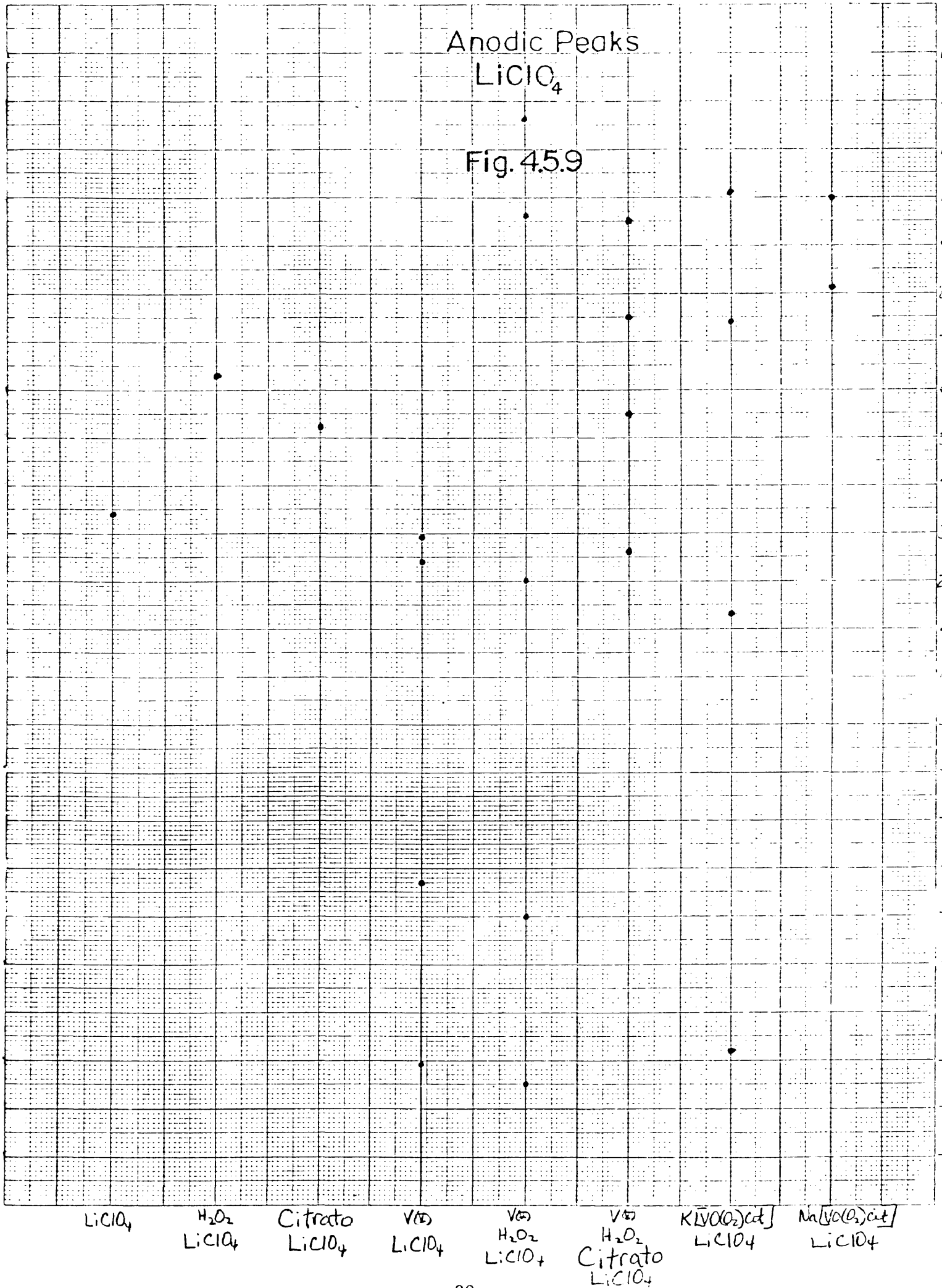
DJM p.129 2000

5-29-84

Cathodic Peaks
$LiClO_4$

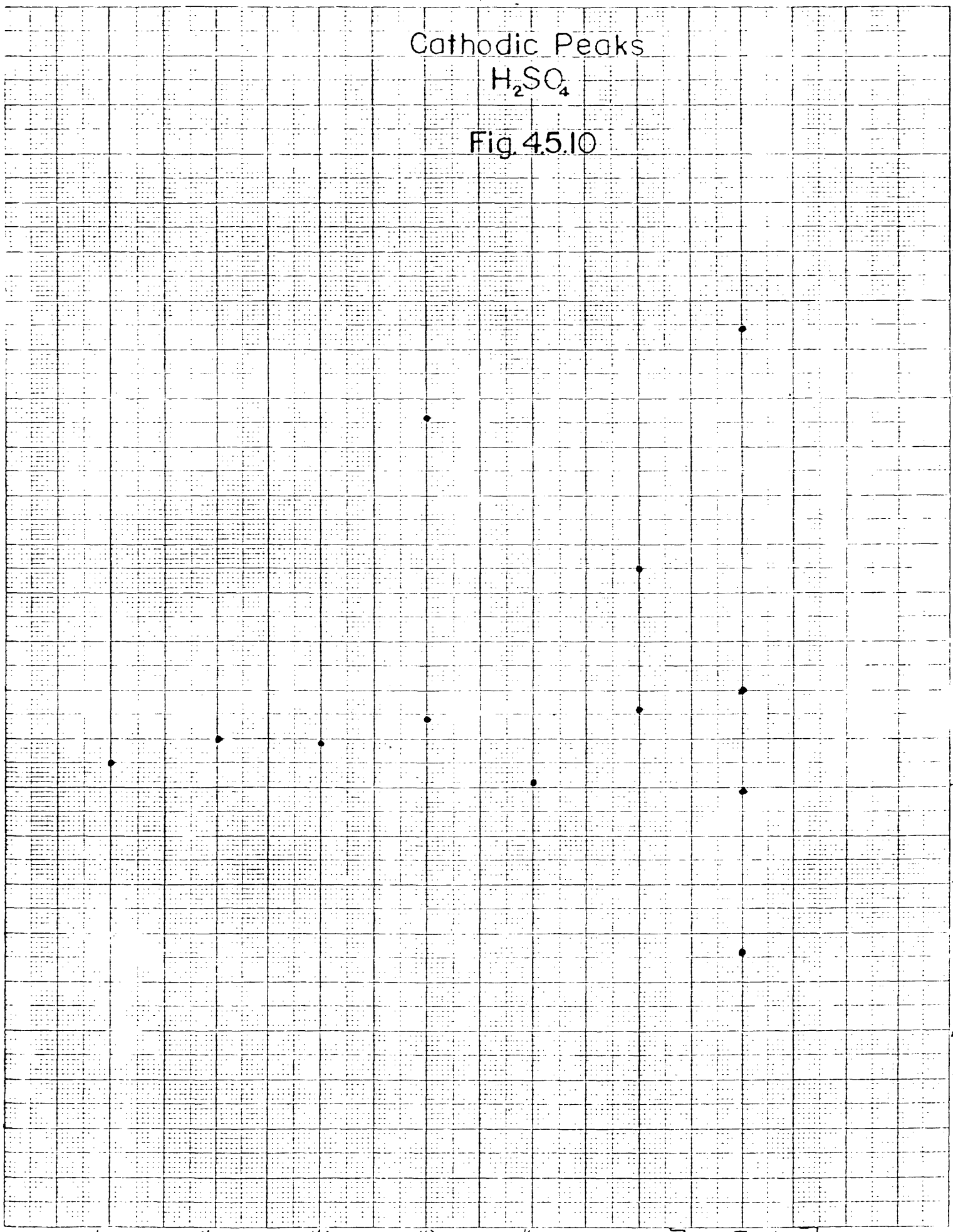
Fig. 4.5.8




Anodic Peaks
$LiClO_4$
Fig. 4.5.9
$LiClO_4$
H_2O_2 $LiClO_4$
Citrato $LiClO_4$
V(V) $LiClO_4$
V(V) H_2O_2 $LiClO_4$
V(V) H_2O_2 Citrato $LiClO_4$
$K[V(O)(O_2)cit]$ $LiClO_4$
$Na[V(O)(O_2)cit]$ $LiClO_4$

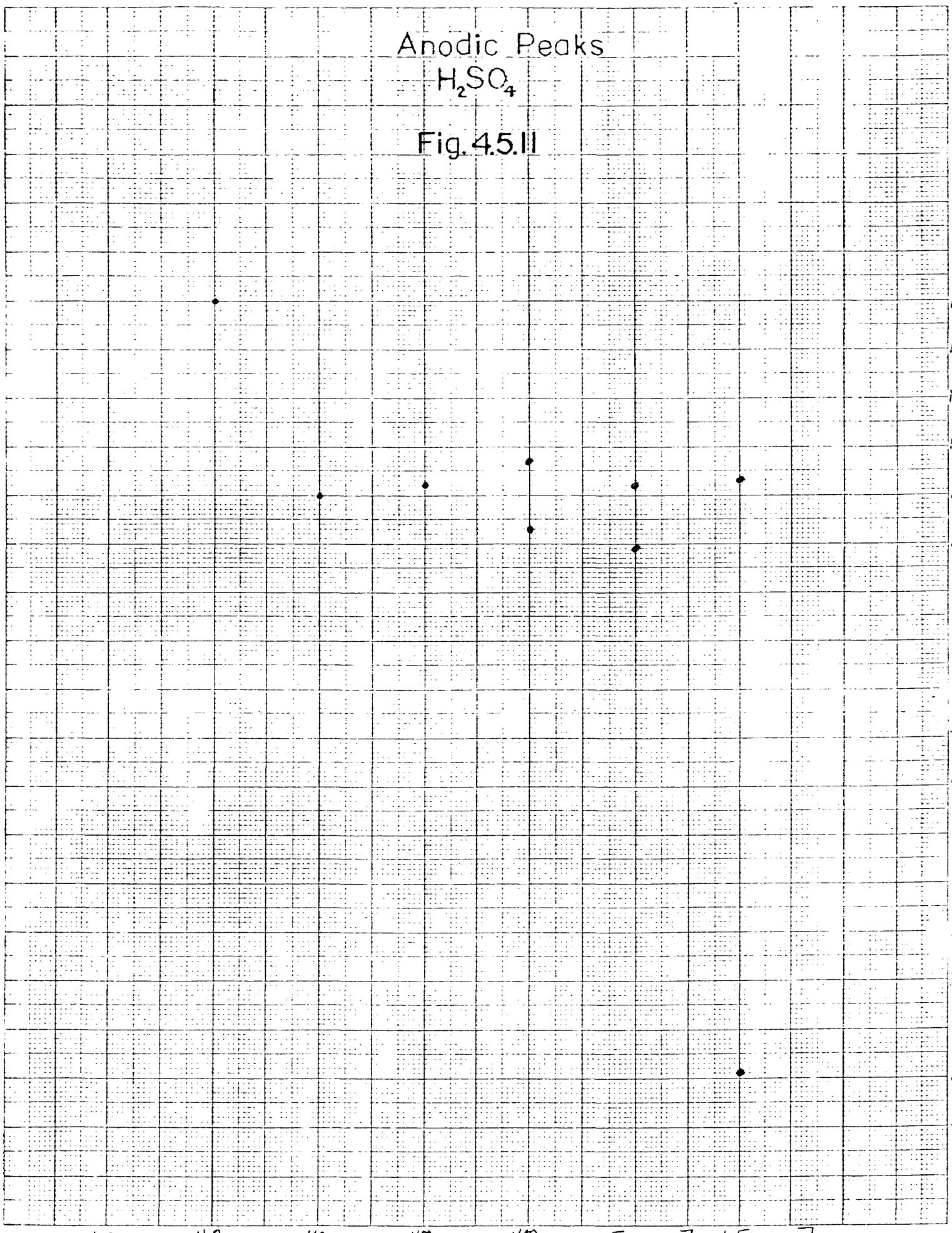
Cathodic Peaks
H_2SO_4

Fig. 4.5.10



Anodic Peaks
H_2SO_4

Fig. 4.5.11



4.6 PEROXO TARTRATO VANADATES

The oxoperoxotartrato vanadate of the formula K[VO(O_2) tartrato]^{34} is a new compound and its structure is not known. In aqueous solution, it most likely rearranges. The electroactive species in the range +1.4 to -1.6V include V(V)/V(IV) and possibly V(IV)/(III) species as well as the tartrate ion since voltammograms of these solutions show peaks in this range.

Figure 4.6.1 shows a cyclic voltammogram of an aqueous solution of K[VO(O_2)tartrato] (~x10^{-3}M) in 0.2M $LiClO_4$. Three cycles are shown (curves 1, 2 and 3). The starting potential was approximately 500mV. The initial scan was cathodic.

To compare the electrochemical behavior of this complex in aqueous solution with the electrochemistry of V(V) in analogous systems, voltammograms shown in figures 4.1.1 through 4.1.8 and 4.6.3 through 4.6.6 were taken.

From the cyclic voltammograms of the various systems and the plots of the peak potentials, the following observations are made.

1) In the $LiClO_4$ solution, (0.2M) pH = 2.8, the peak potentials of the compound in solution differ significantly from those of the solution made from components. This is especially true of the anodic scans. Apparently, under these conditions and time scale, the mixture of components does not form the same reactive species as does the compound when dissolved in $LiClO_4$.

2) On comparing initial anodic and cathodic scans for the compound in $LiClO_4$ (fig.4.6.1 and 4.6.2), one can see an absence of a peak at approximately 650mV on the first cycle of an anodic scan. This peak appears after a cycle has been completed. This suggests the peak is due to the oxidation of a species that must first be generated by a cathodic scan.

3) In acid solutions the peak potentials of the compound match very closely the peak potentials of the solution made of components. This suggests that under these acidic conditions, the compound undergoes final rearrangement or more probably some degree of decomposition.

On comparing the voltammograms of the various solutions run, the following characteristic shifts in peak potentials is observed.

Vanadium (V/IV) $E_{p(c)}$ peaks at approximately 50 and 200mV show a general trend to more positive values (see fig. 4.6.7) when peroxide, then peroxide and tartaric acid is added to vanadium. However, this trend is reversed on the voltammogram of the compound.

These results show that vanadium (V/IV) peaks are affected by the presence of ligands and the degree of bonding to the ligand.

Initial pH = 2.0

Very Fresh C.V. of Sample

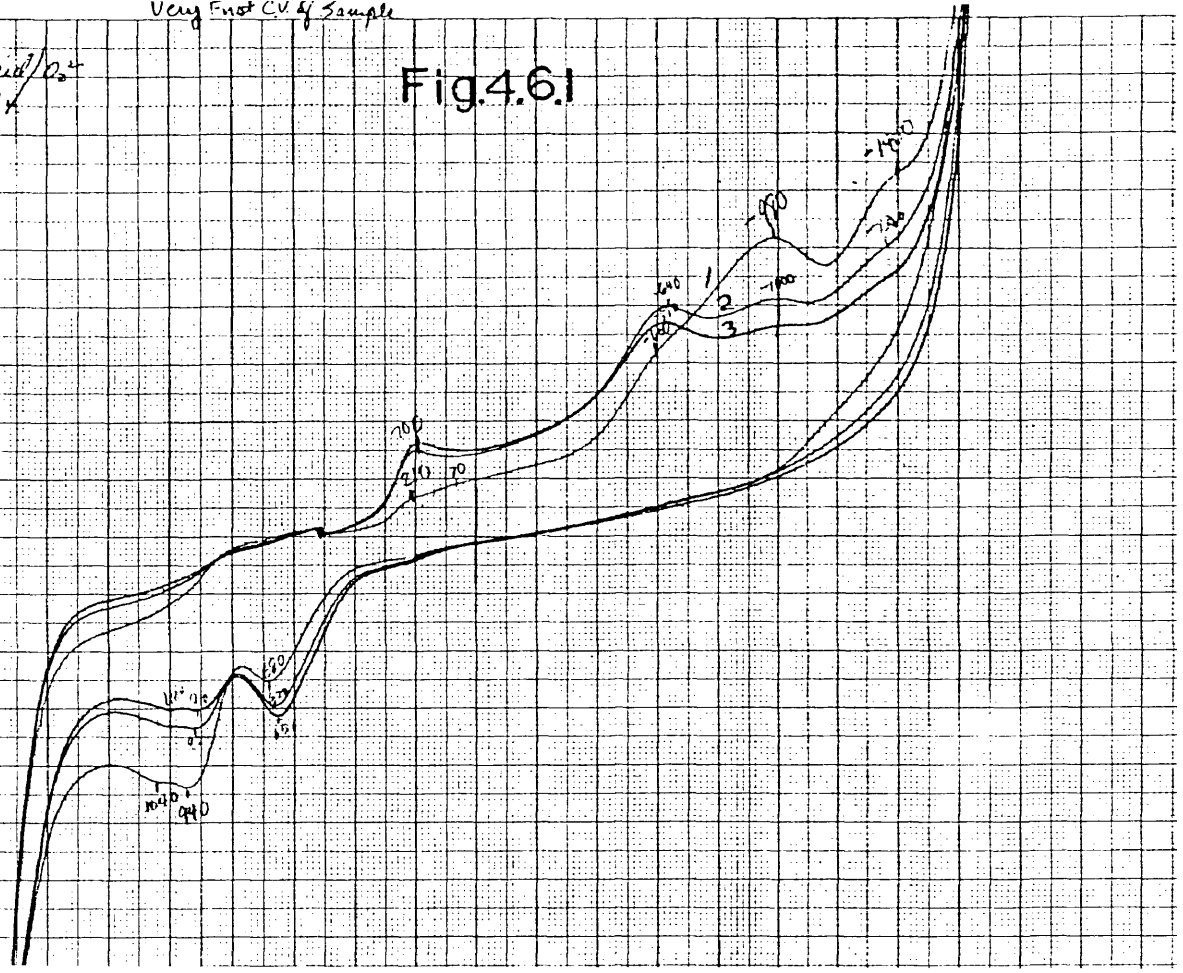
30.7mg K/V/Tartaric Acid/O_2^{2-} in 15ml 0.2M LiClO4

x = 200mv/div

y = 10uA/div

Scan rate = 100mv/sec

Fig.4.6.1



pH = 2.77

Reverse Scan

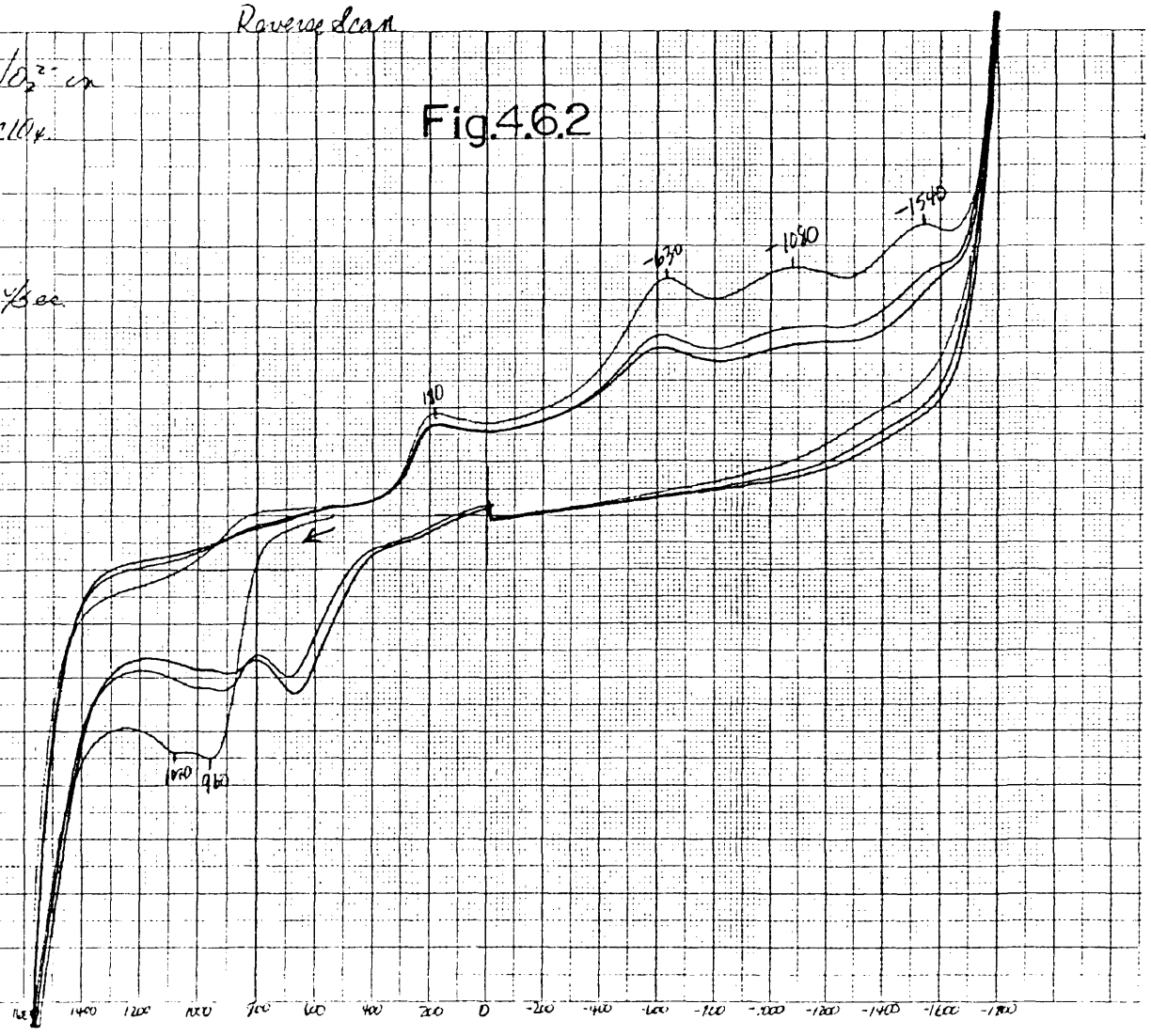
30.3mg K/V/Tar/O_2^{2-} in 15ml 0.2M LiClO4

x = 200mV/div

y = 10uA/div

Scan rate = 100mv/sec

Fig.4.6.2



DJM p121

1-13-94

Fig.4.6.3

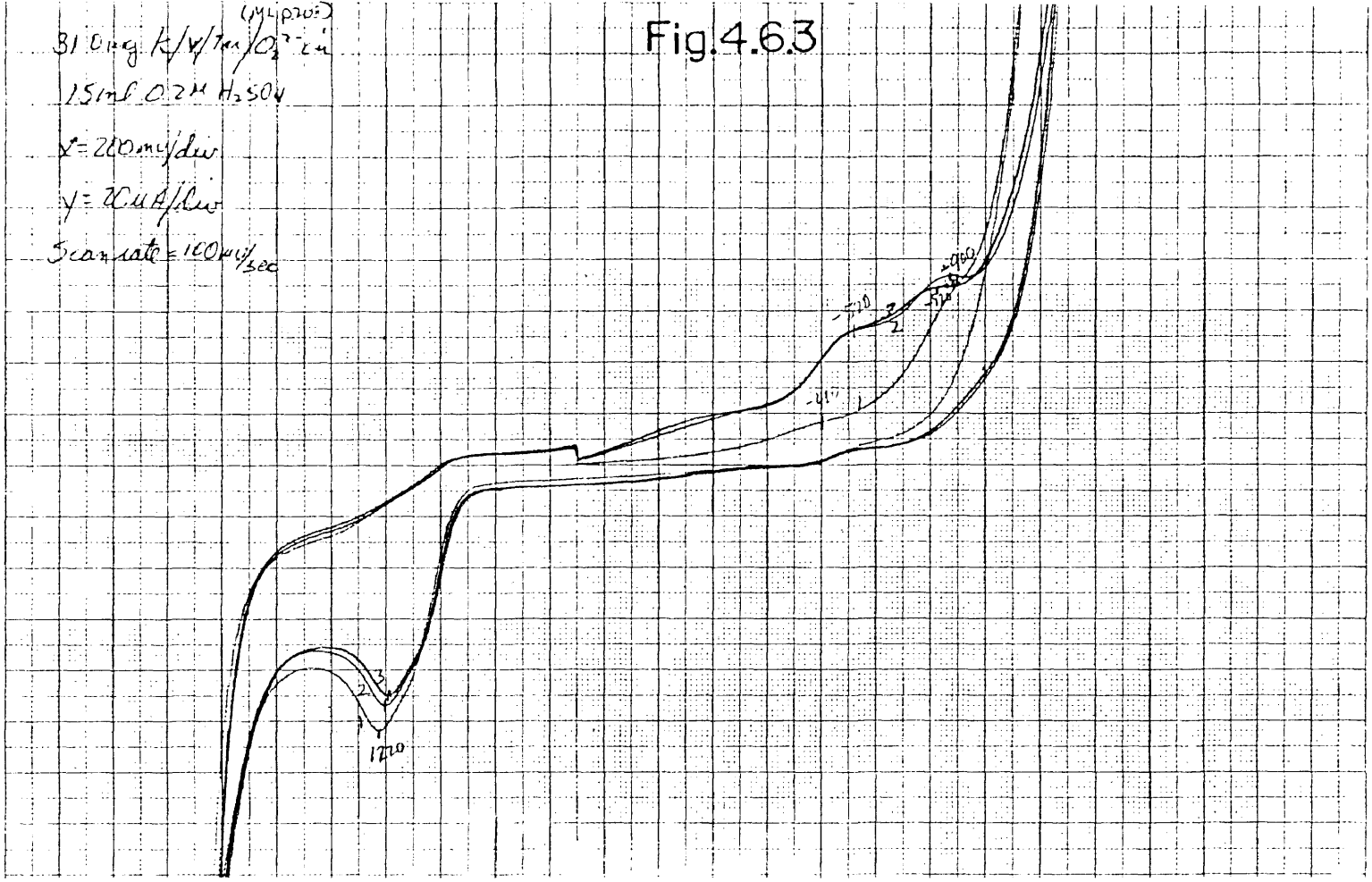
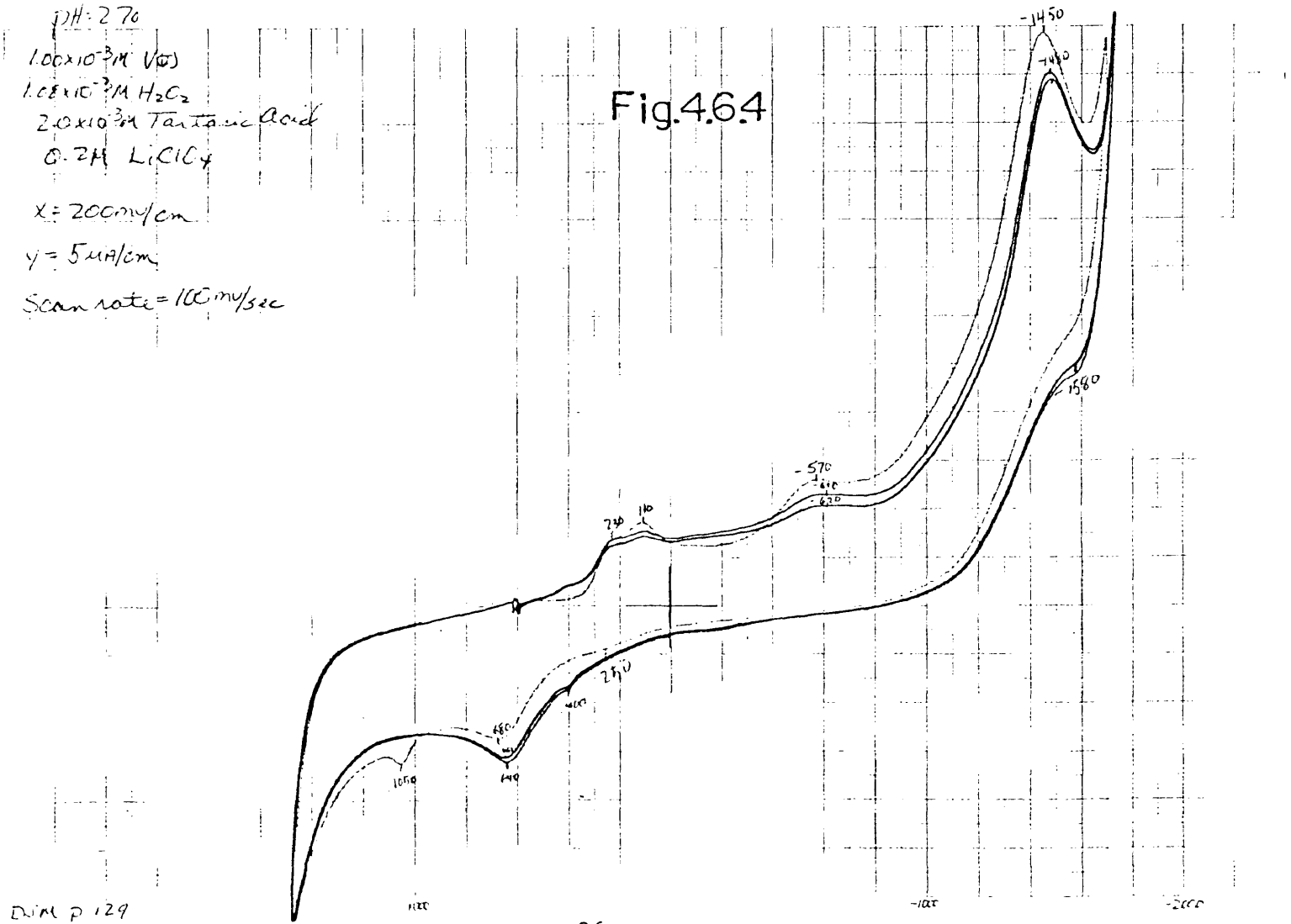


Fig.4.6.4



DVM p 129
5-24-84

1.00×10^{-3}M VO(

1.08×10^{-3}M H_2O_2

2.0×10^{-3}M Tartaric Acid

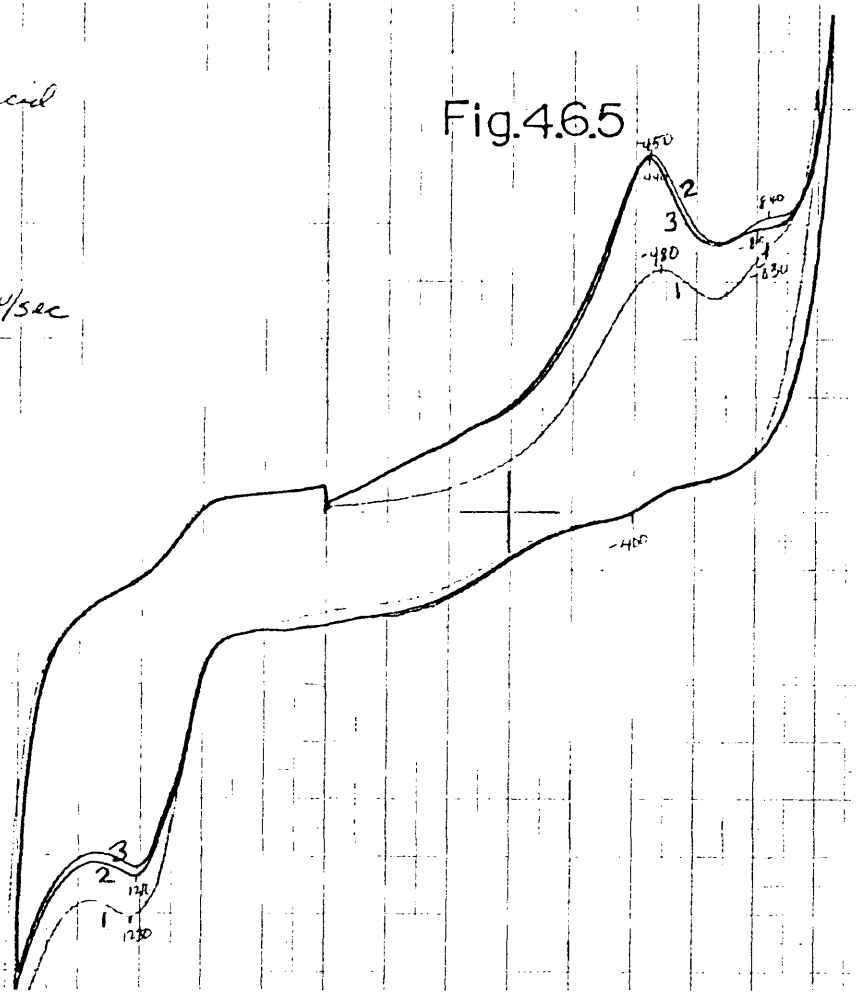
0.2M H_2SO_4

X = 200mv/cm

Y = 5μA/cm

Scan rate = 100mv/sec

Fig. 4.6.5



pH = 2.88

2.0×10^{-3}M Tartaric Acid

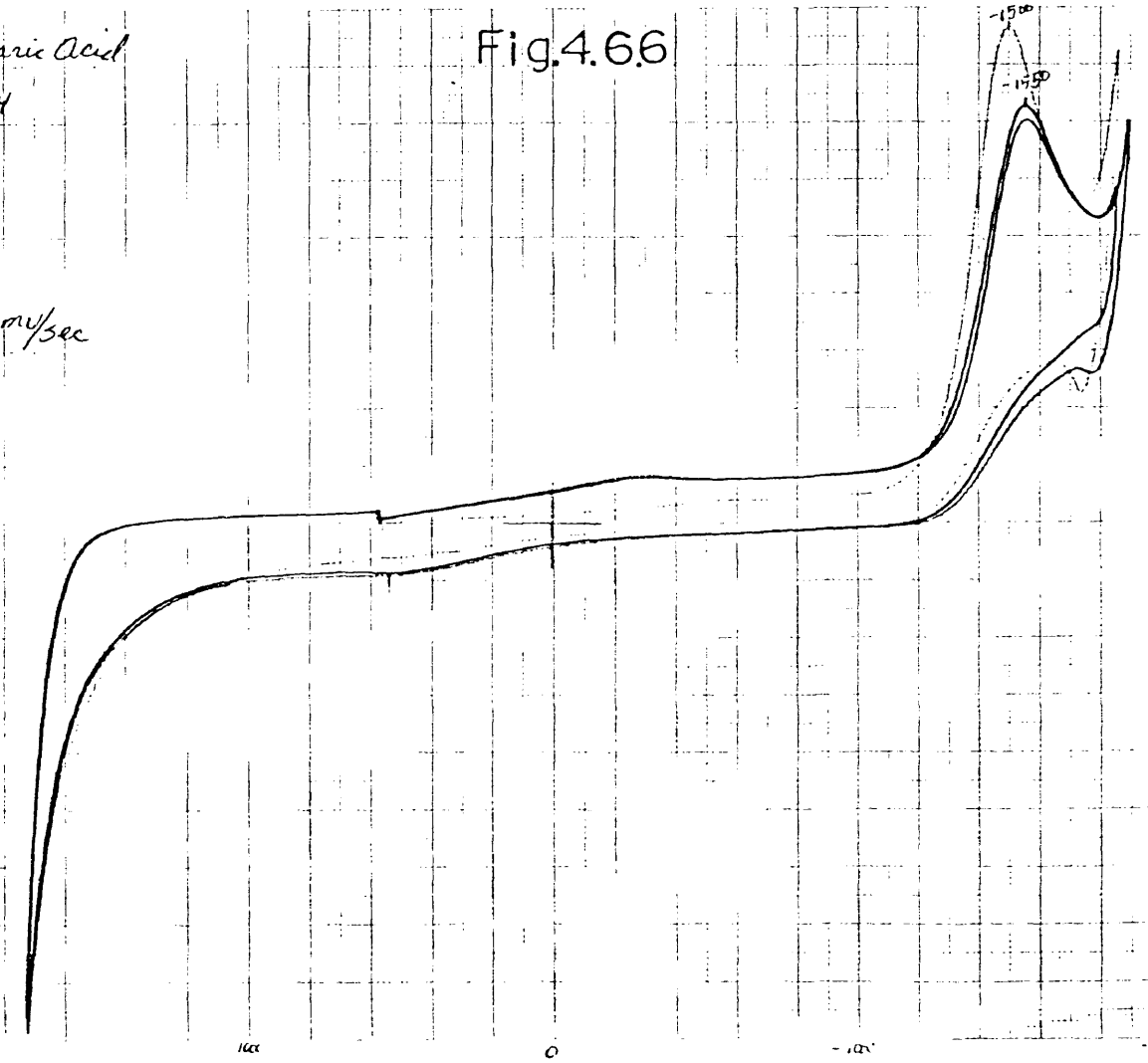
0.2M $LiClO_4$

X = 200mv/cm

Y = 10μA/cm

Scan rate = 100mv/sec

Fig. 4.6.6



Blank $LiClO_4$ soln.

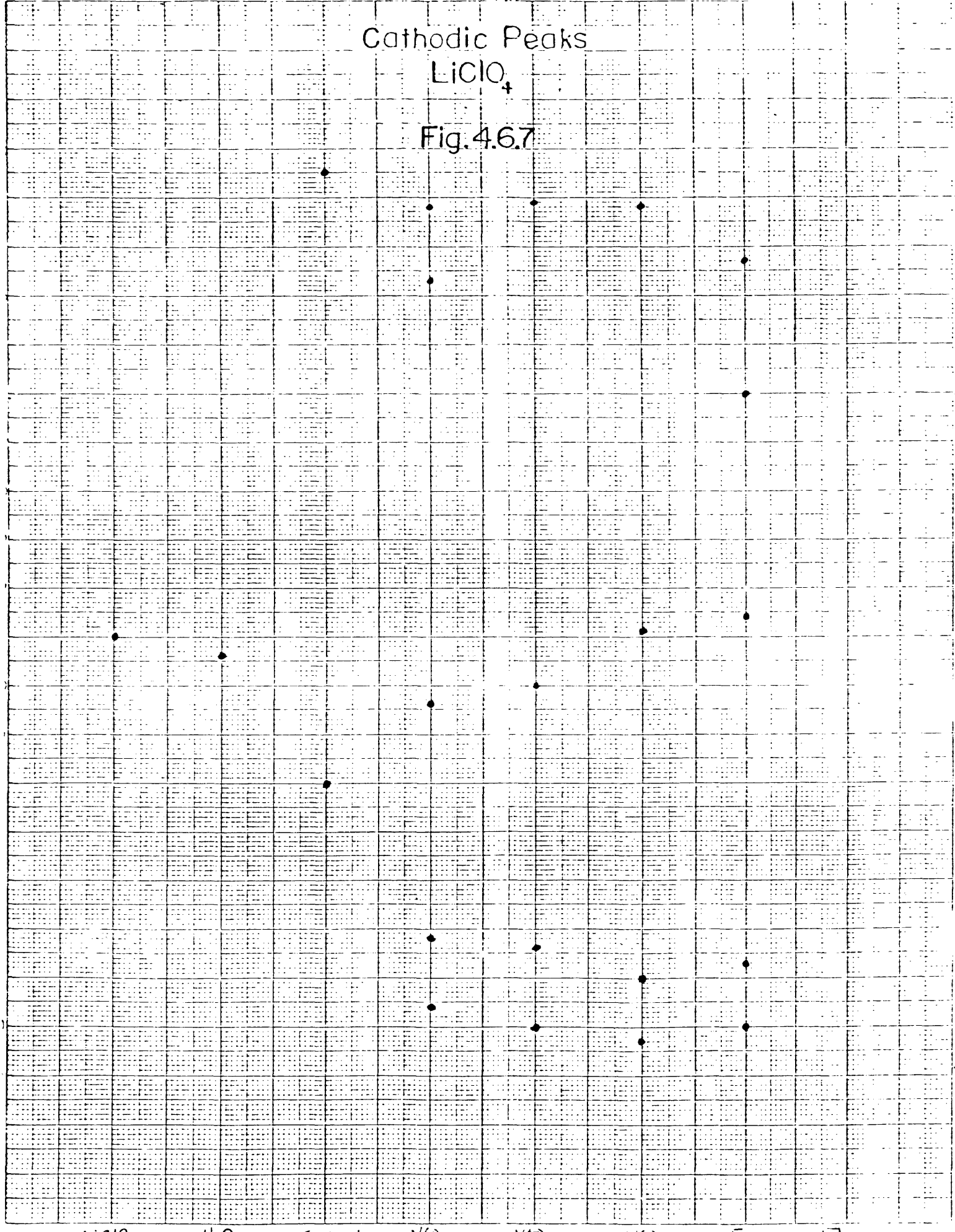
with Citric Acid

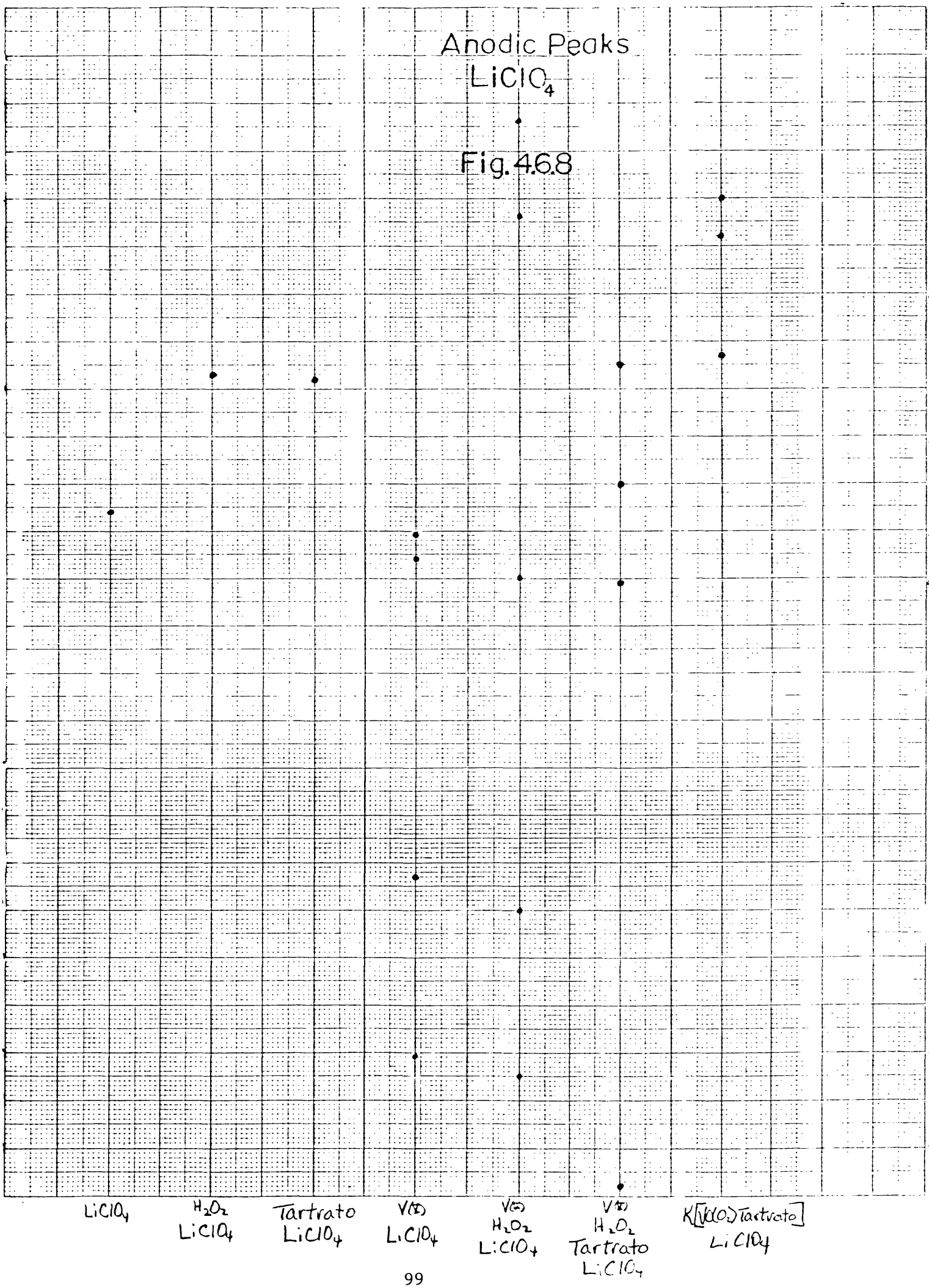
DJH P129

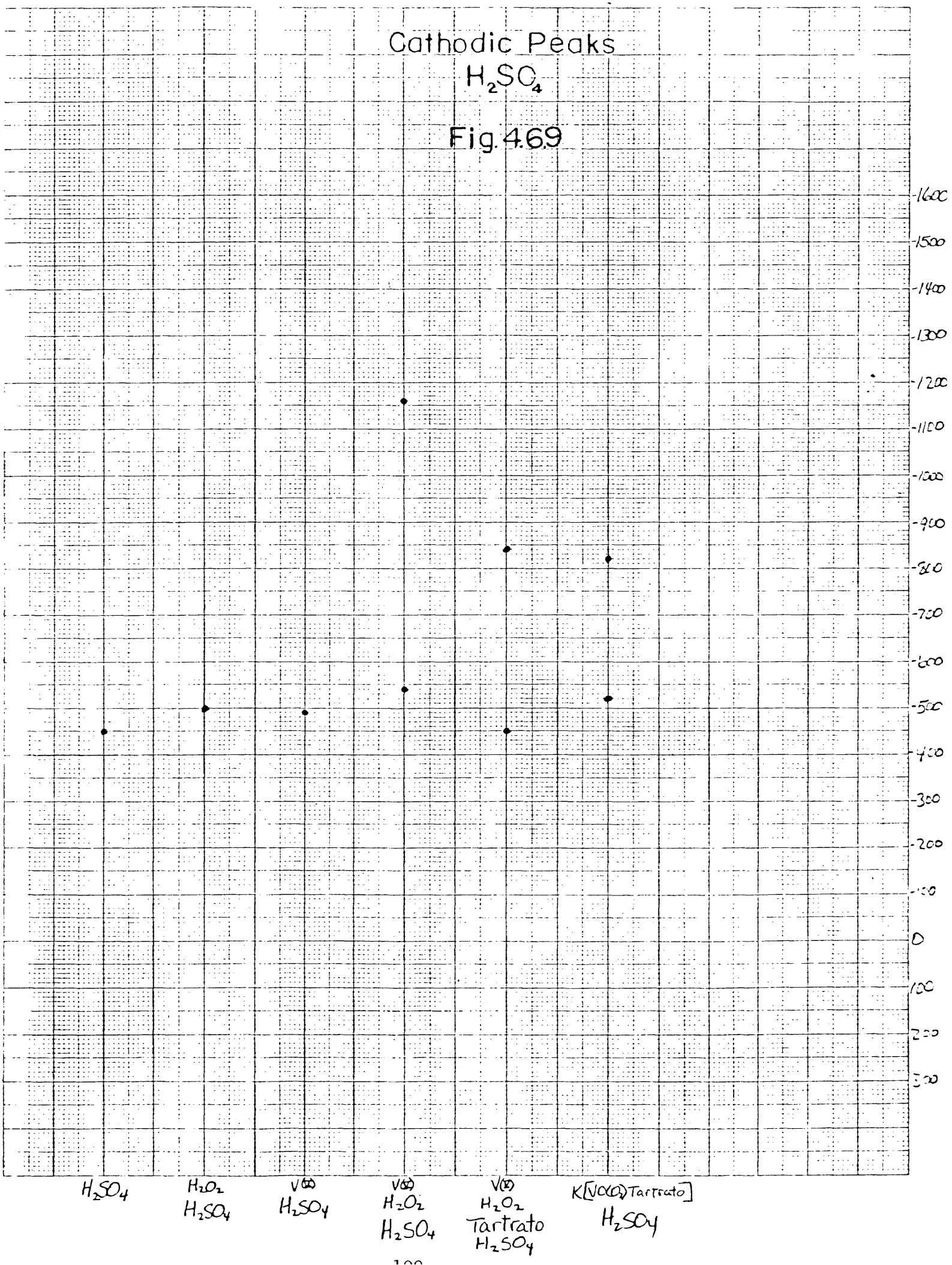
5-26-84

Cathodic Peaks
$LiClO_4$

Fig. 4.6.7

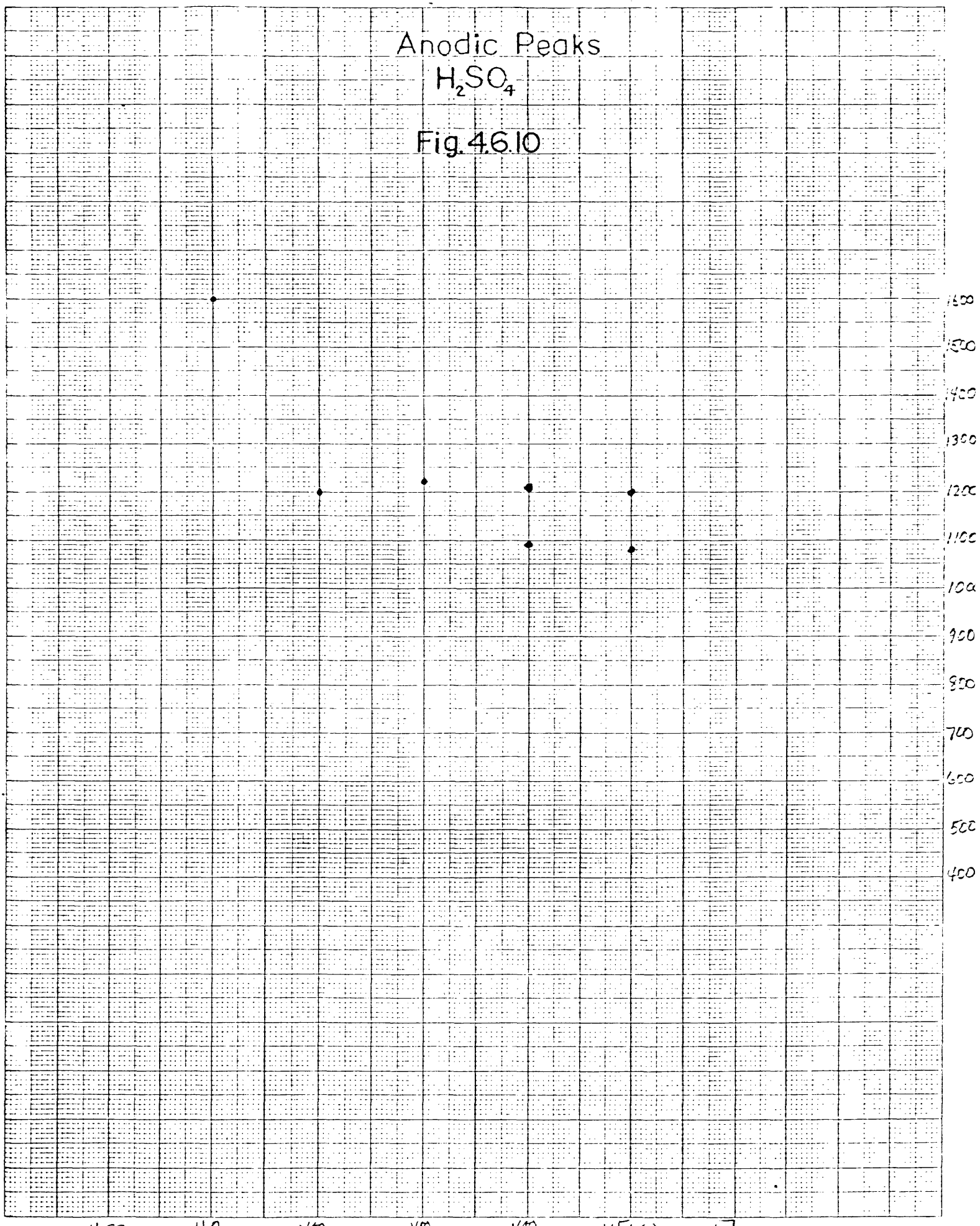



Anodic Peaks
$LiClO_4$
Fig. 4.6.8
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-13
-15
$LiClO_4$
H_2O_2 $LiClO_4$
Tartrato $LiClO_4$
V(v) $LiClO_4$
V(v) H_2O_2 $LiClO_4$
V(v) H_2O_2 Tartrato $LiClO_4$
K[VO(O$_2$)Tartrato] $LiClO_4$


Cathodic Peaks
H_2SO_4
Fig. 4.69
-1600
-1500
-1400
-1300
-1200
-1100
-1000
-900
-800
-700
-600
-500
-400
-300
-200
-100
0
100
200
300
H_2SO_4
H_2O_2 H_2SO_4
V(IV) H_2SO_4
V(IV) H_2O_2 H_2SO_4
V(IV) H_2O_2 Tartrato H_2SO_4
K[VO(O)Tartrato] H_2SO_4

Anodic Peaks
H_2SO_4

Fig. 4.6.10



4.7 PEROXO NTA VANADATES

The oxoperoxo NTA vanadate of the formula $K_2[VO(O_2)NTA]$[18] is a new compound and its structure is known. In aqueous solution it most likely rearranges. The electroactive species in the range +1.6 to -1.6V include V(V/IV) and possibly V(IV/III) species as well as the NTA ion since voltammograms of these solutions show peaks in this range.

Figure 4.7.1 shows a cyclic voltammogram of an aqueous solution of $K_2[VO(O_2)NTA]$ ($\sim x10^{-3}M$) in 0.2M $LiClO_4$. Three cycles are shown (curves 1, 2 and 3) and a 0.2M $LiClO_4$ blank. The initial potential was 600mV and the scan direction was cathodic.

To compare the electrochemical behavior of this compound in aqueous solution with the electrochemistry of V(V) in analogous systems, voltammograms shown in figures 4.1.1 through 4.1.8 and 4.7.2 through 4.7.5 were taken.

From the cyclic voltammograms of the various systems, the plots of the peak potentials, and the potentiometric titrations, the following observations are made:

1) In 0.2M $LiClO_4$ and pH≈6.7 the cyclic voltammogram of the potassium salt shown similarities and

differences in the peak potentials as compared to the mixture of component solutions. Both voltammograms (fig. 4.7.1 and 4.7.3) show a cathodic peak near -1530mV and an anodic peak near -1350mV. These peaks match closely to peak present at these positions on the voltammogram of vanadium (V)+H_2O_2 in 0.2M $LiClO_4$ (fig. 4.1.4). This information implies that under these conditions and time frame, this compound and the mixture of component solutions form an electroactive species of the same cathodic potential as peroxovanadates(V) in the absence of a heteroligand.

2) The dramatic change in the number anodic peaks with successive cycles for the NTA compound (Fig. 4.7.1) indicate that chemical reactions occur during the scan.

3) On comparing the V(V/IV) or V(IV/III) peaks near -1530mV (on the cathodic scan) and -1350mV (on the anodic scan) one sees a slight trend toward more negative values for the cathodic peak for the series of V(V), V(V)+H_2O_2+NTA, then $K_2[VO(O_2)NTA]$ and essentially no trend for the anodic peak (see fig. 4.7.6).

4) In 0.2M H_2SO_4 the number and position of peaks present on the voltammogram of the K-salt appear

to be similar to those present on the voltammogram of the mixture of components. This implies that under these conditions of high acidity, the compound rearranges.

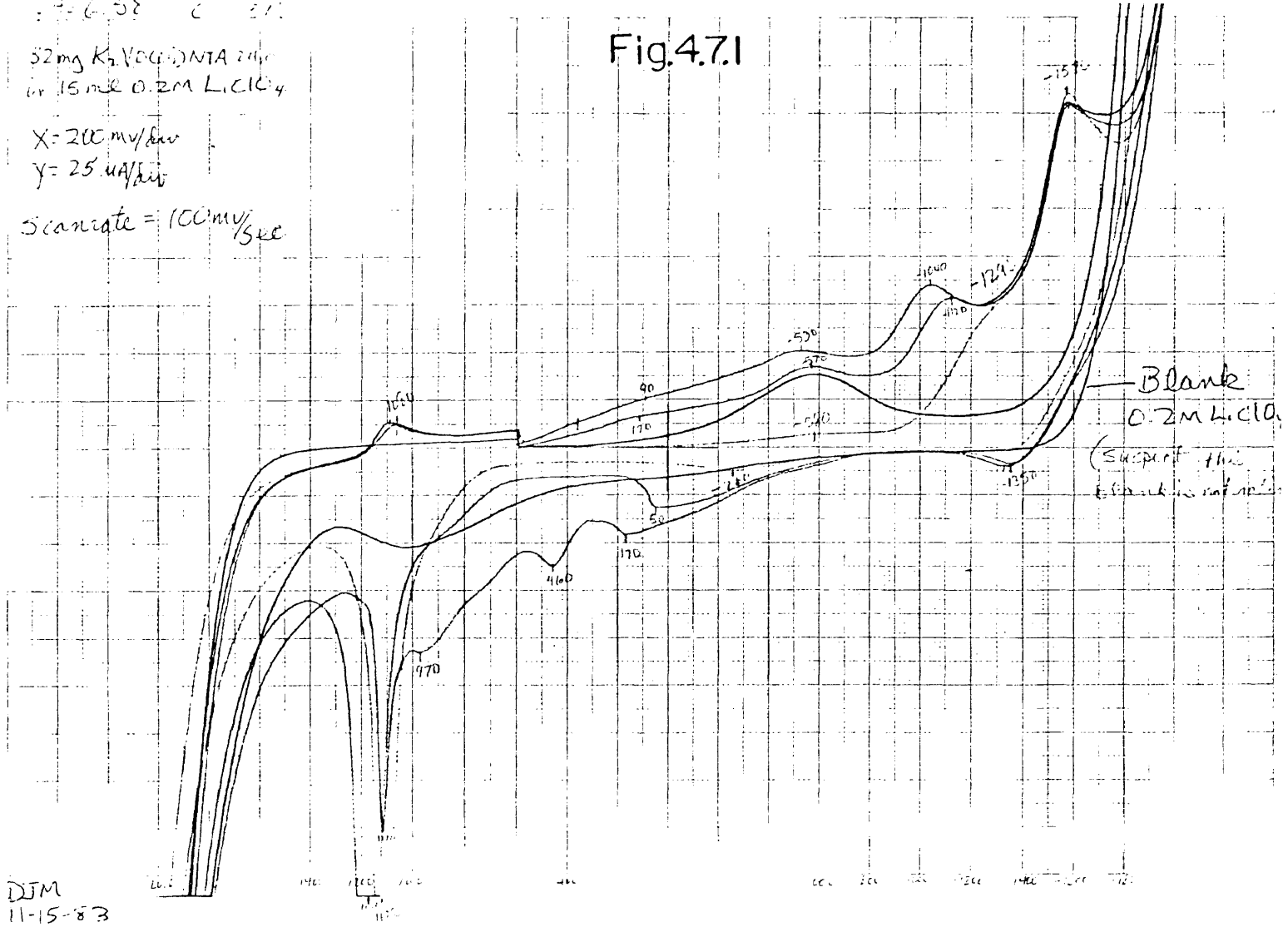
5) The potentiometric titrations show good agreement in the stoichiometry for all the compounds titrated. The type of salt did not appear to have any effect on the titration curve or the potentials at which characteristic points occur. The solutions of the compounds did not behave the same as the mixture of components in acid solution.

Fig.4.7.1

52 mg $K_2VO(C_2)NTA$ 2H$_2$O
in 15 mL 0.2M $LiClO_4$

X = 200 mV/div
Y = 25 uA/div

Scan rate = 100 mV/sec



DJM
11-15-83

Fig.4.7.2

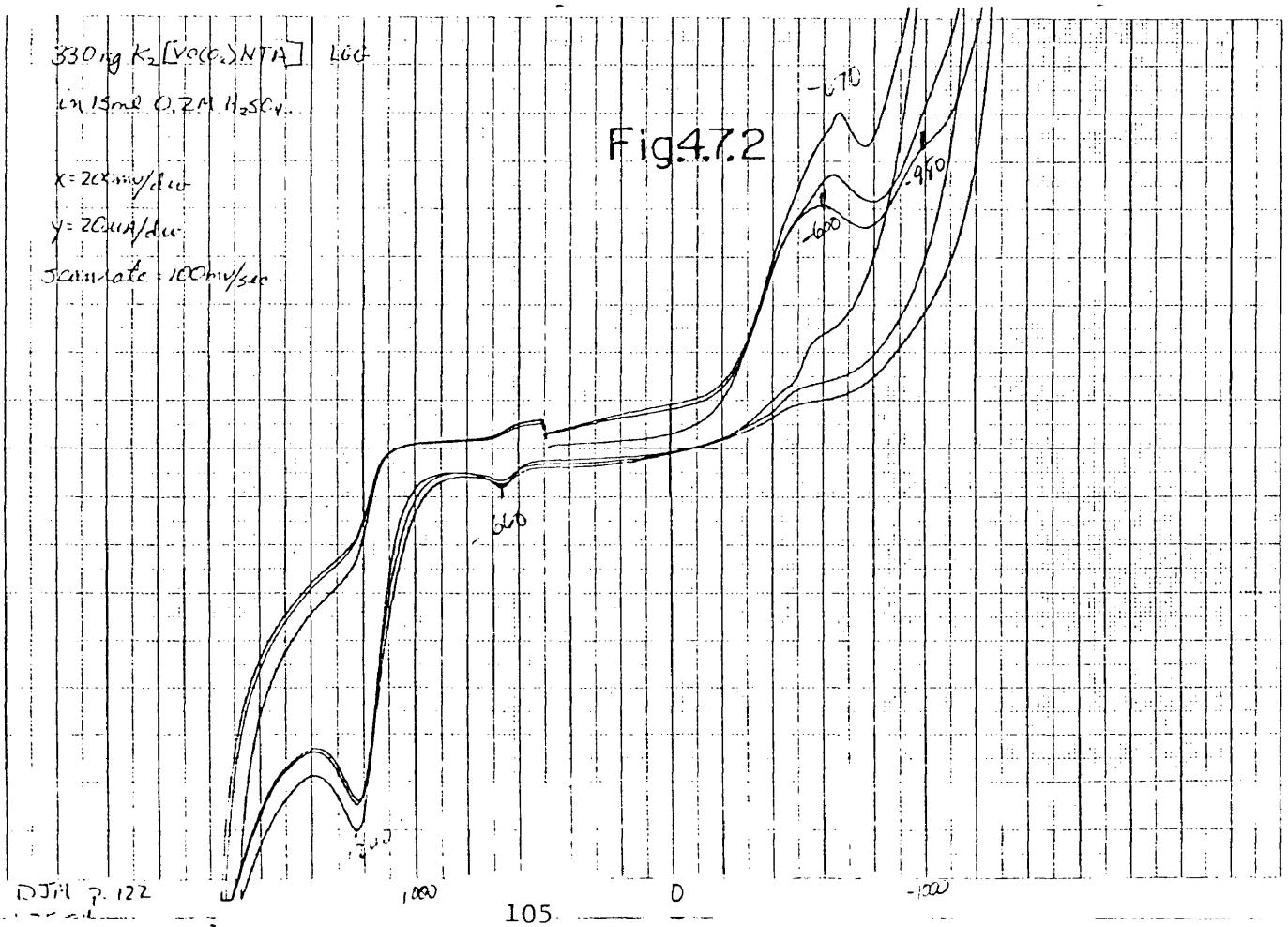
330 mg $K_2[VO(C_2)NTA]$ 4H$_2$O

in 15 mL 0.2M H_2SO_4

X = 200 mV/div

Y = 20 uA/div

Scan rate = 100 mV/sec



DJM p. 122

Fig.4.7.3

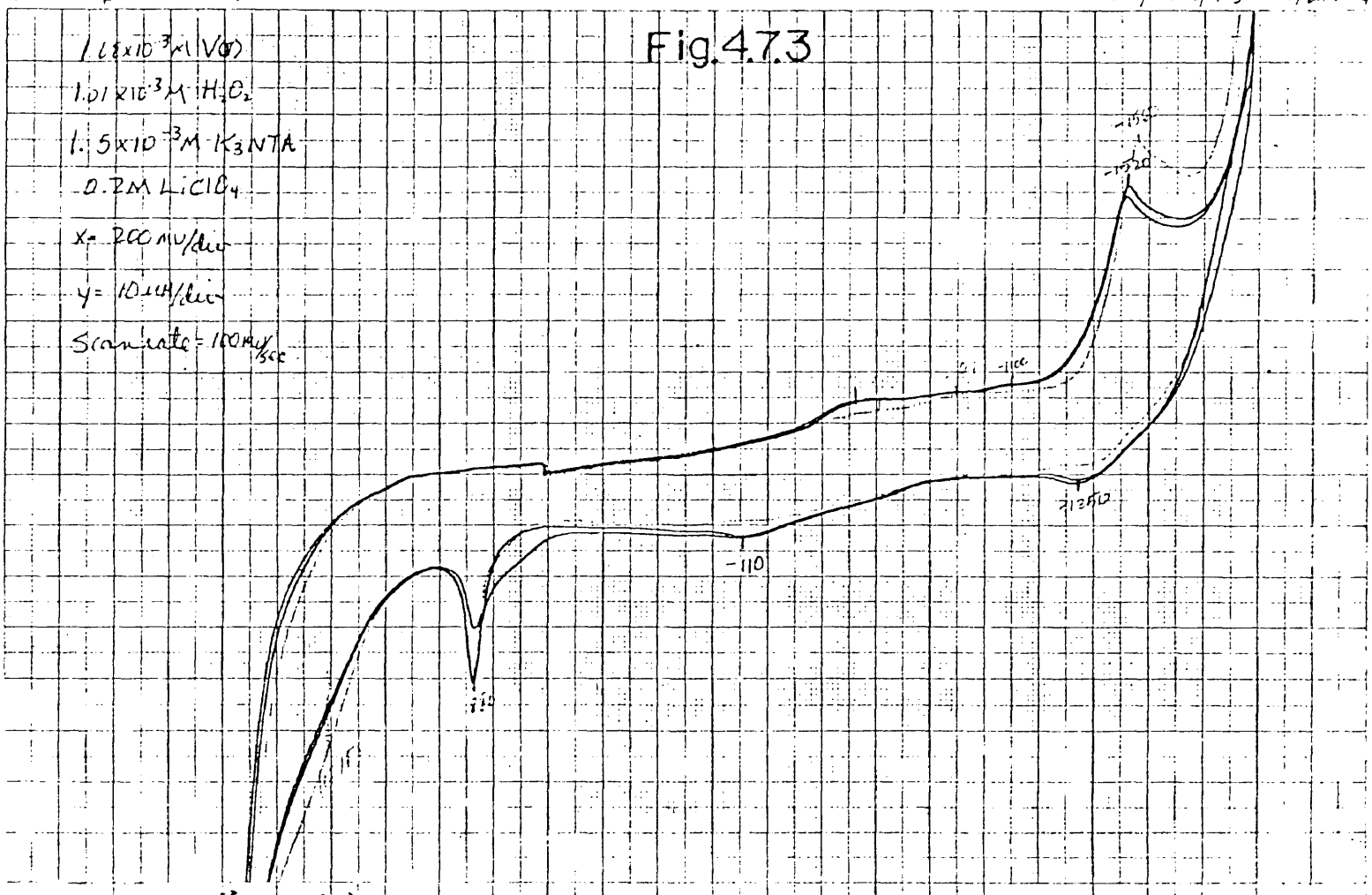
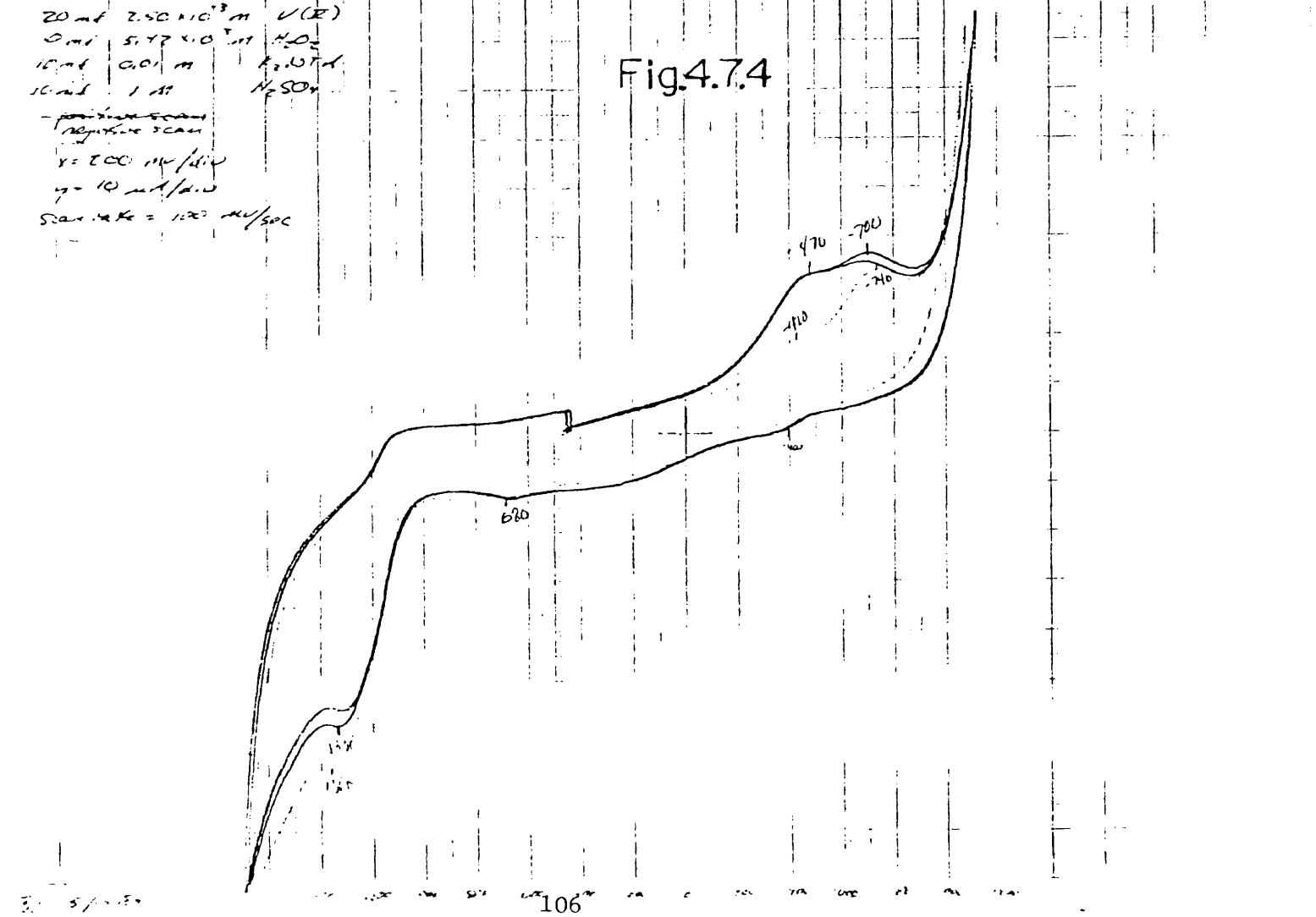


Fig.4.7.4



pH 8.17

2.0×10^{-3}M K_3NTA

0.2M $LiClO_4$

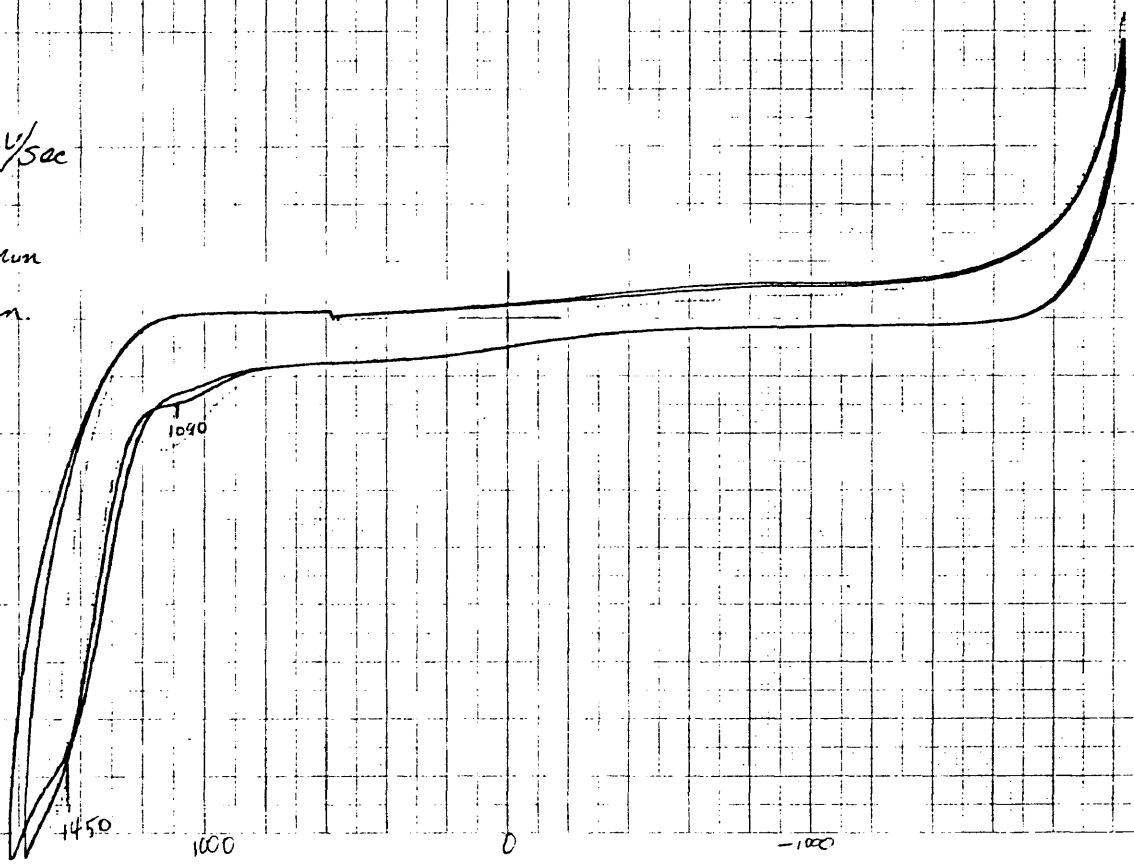
X = 200 mv/cm

y = 10 uA/cm

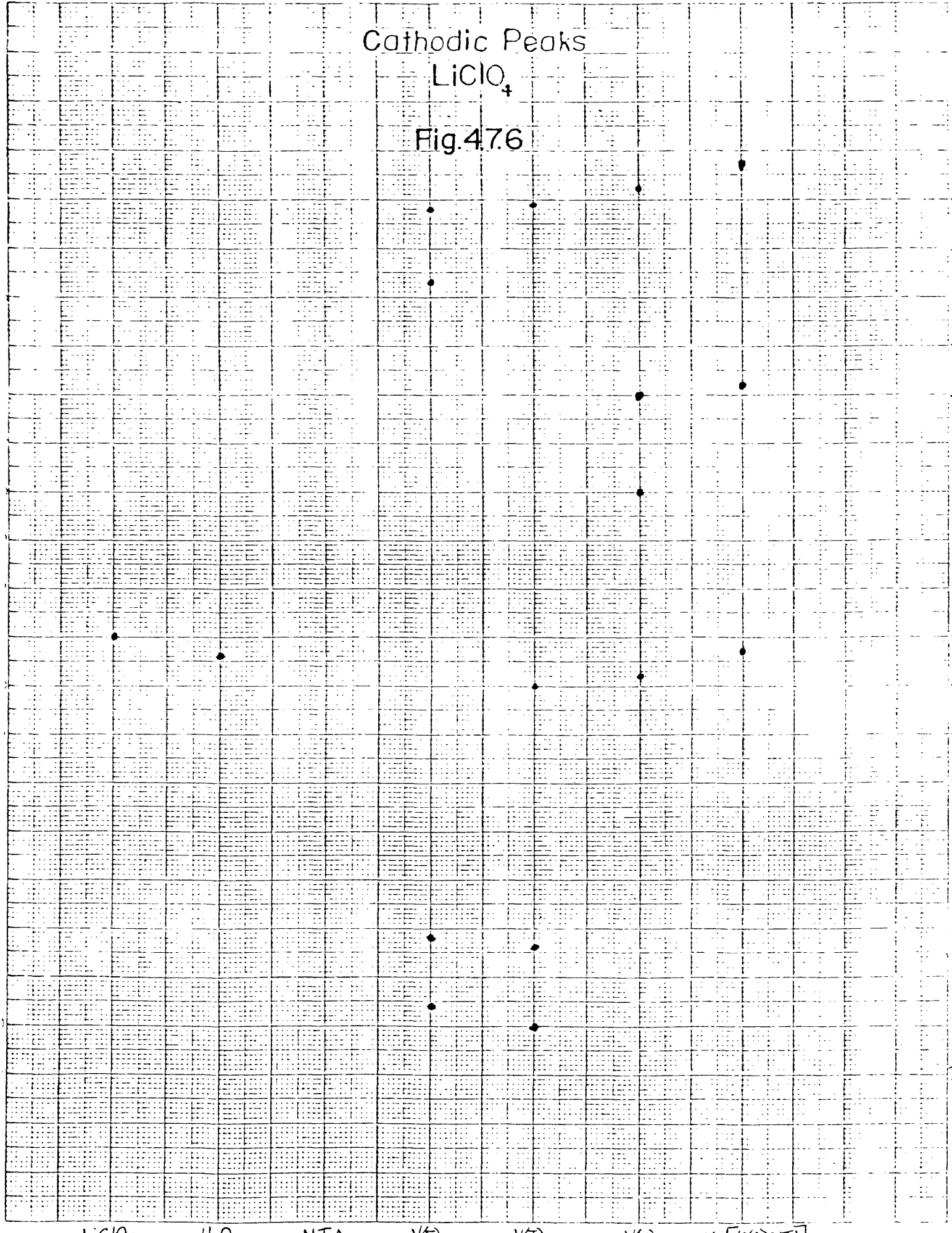
Scan rate = 100 mv/sec

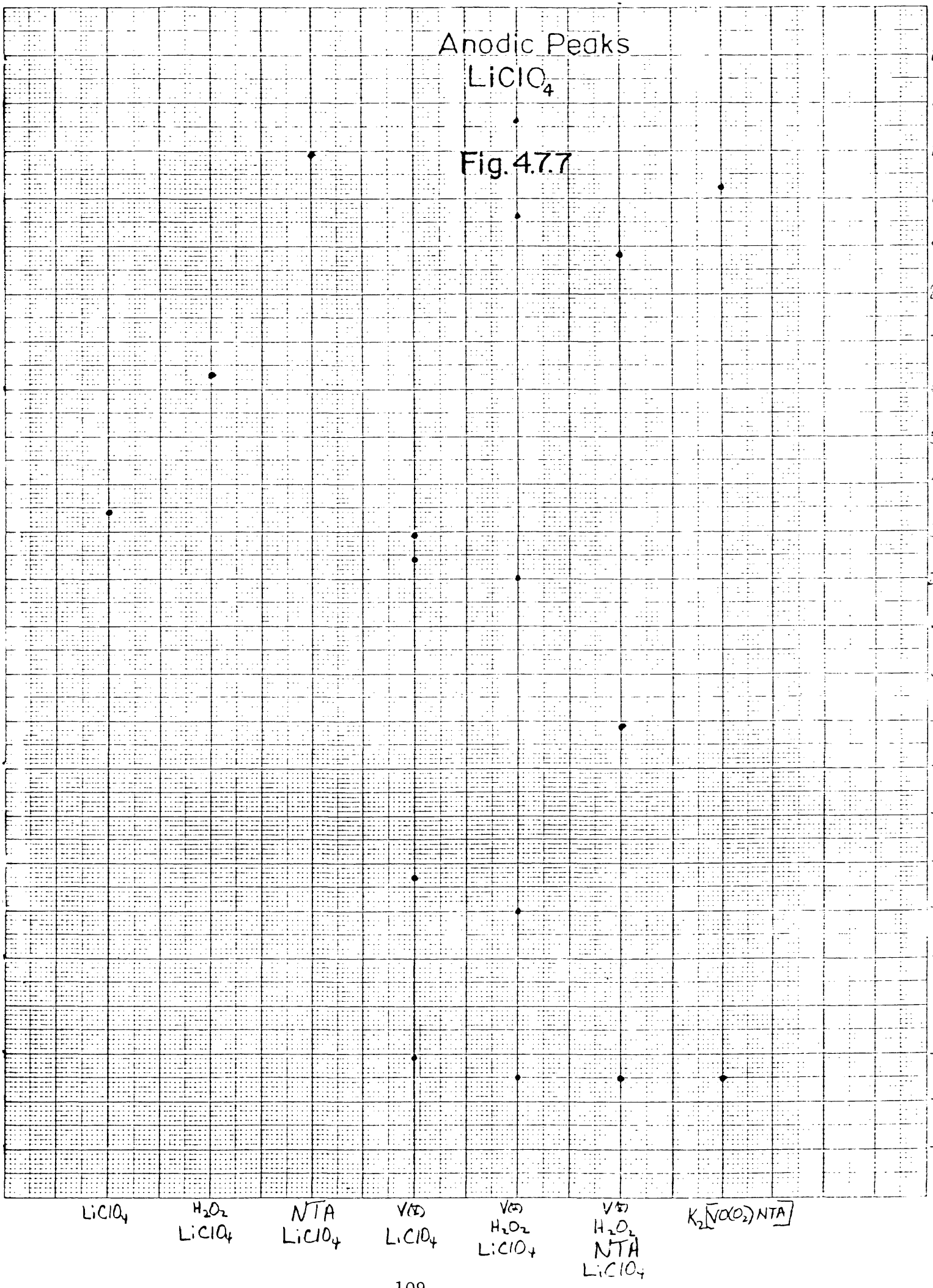
Blank $LiClO_4$ was run on Citric Acid scan.

Fig. 4.7.5



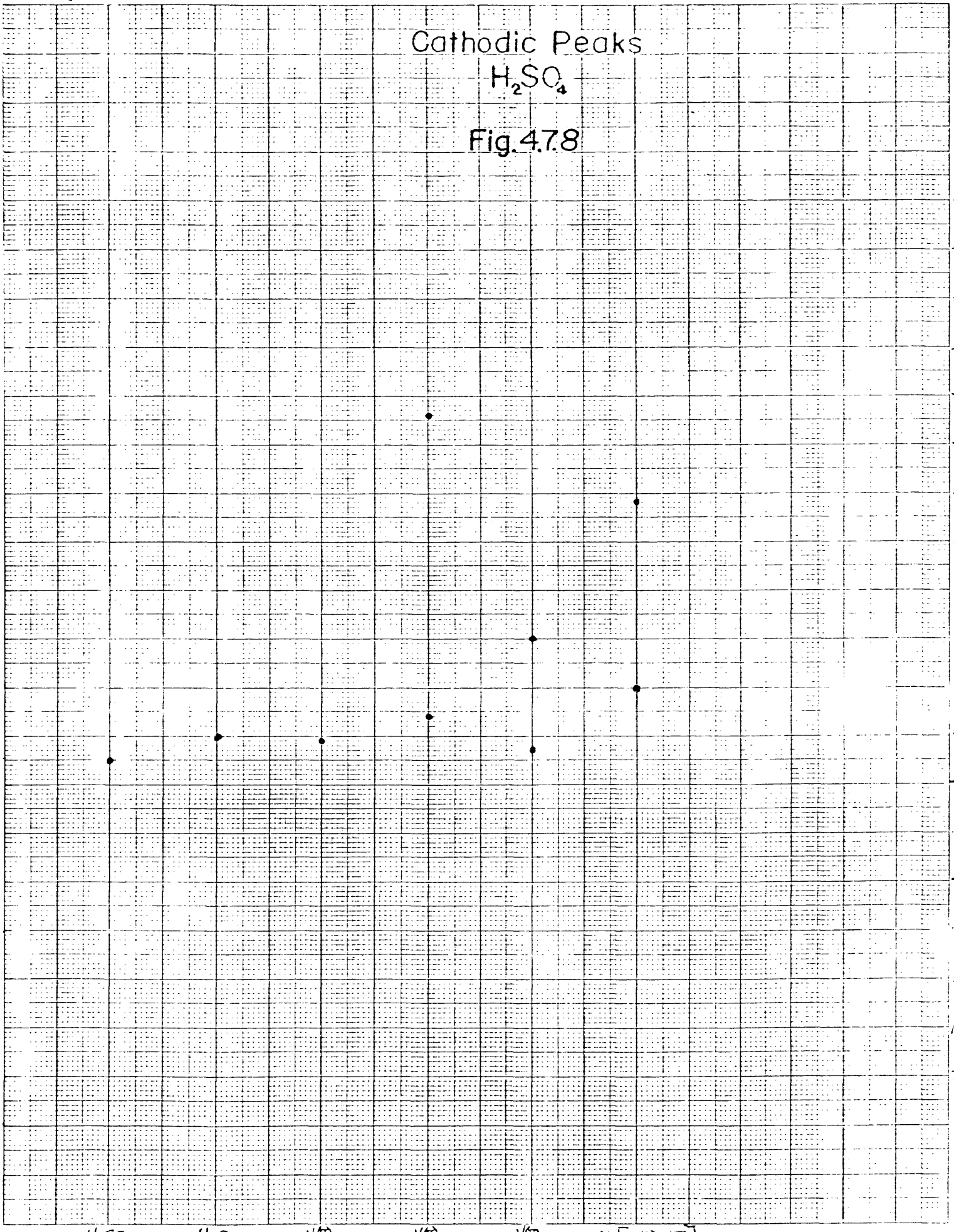
Dom p.129 200
5-29-84

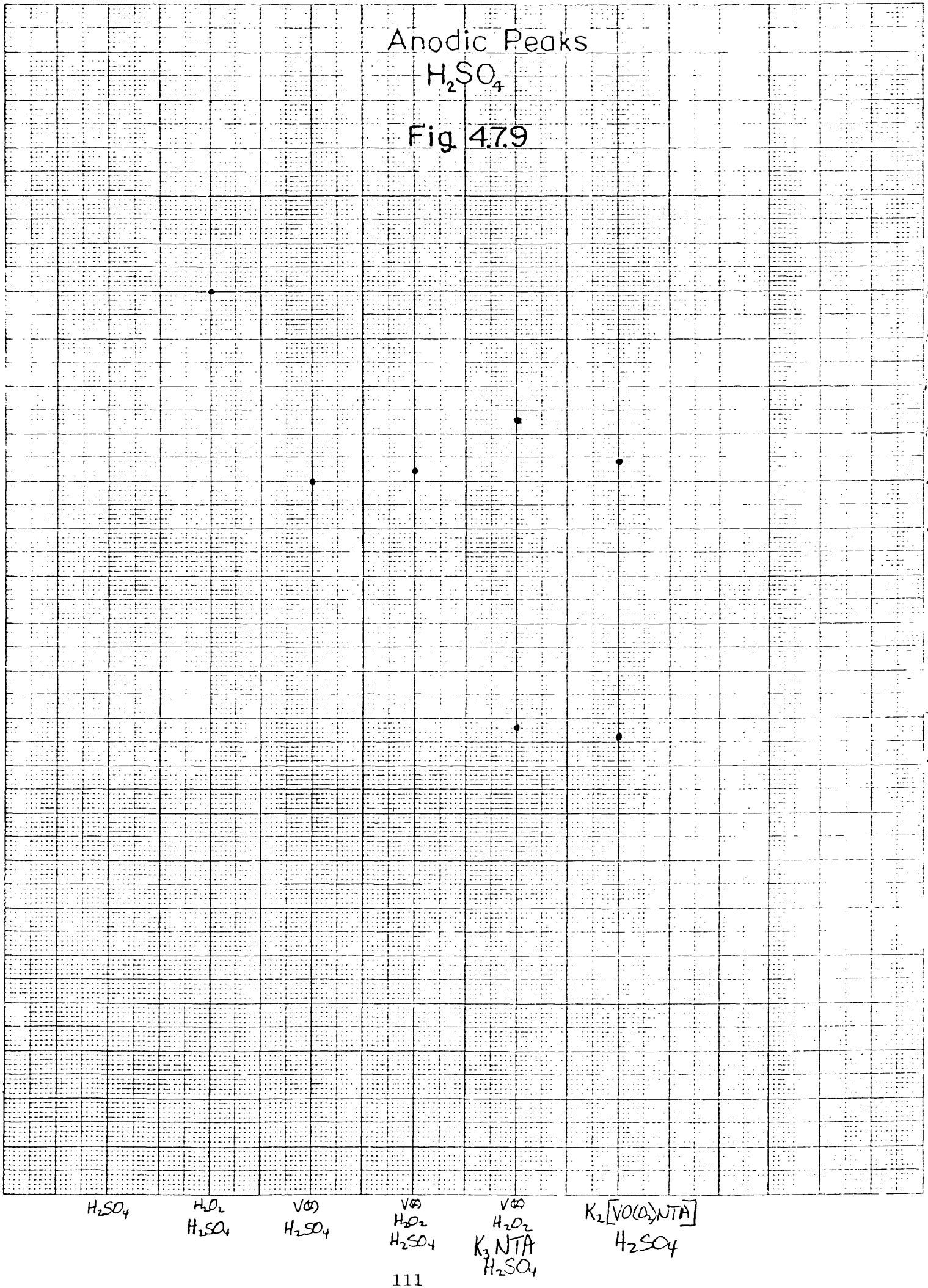

Cathodic Peaks
$LiClO_4$
Fig. 4.7.6
$LiClO_4$
H_2O_2 $LiClO_4$
NTA $LiClO_4$
V(V) $LiClO_4$
V(V) H_2O_2 $LiClO_4$
V(V) H_2O_2 NTA $LiClO_4$
$K_2[VO(O_2)NTA]$ $LiClO_4$


Anodic Peaks
$LiClO_4$
Fig. 4.7.7
$LiClO_4$
H_2O_2 $LiClO_4$
NTA $LiClO_4$
V(IV) $LiClO_4$
V(IV) H_2O_2 $LiClO_4$
V(IV) H_2O_2 NTA $LiClO_4$
$K_2[VO(O_2)NTA]$

Cathodic Peaks
H_2SO_4

Fig. 4.7.8




Anodic Peaks
H_2SO_4
Fig. 4.7.9
H_2SO_4
H_2O_2 H_2SO_4
V(V) H_2SO_4
V(V) H_2O_2 H_2SO_4
V(V) H_2O_2 K_3NTA H_2SO_4
$K_2[VO(O_2)NTA]$ H_2SO_4

4.8 PEROXO EDTA VANADATES

The oxoperoxo EDTA vanadate of the formula $Cs[VO(O_2)EDTA]$ is a new compound and its structure is not known. In aqueous solution, it most likely rearranges. The electroactive species in the range +1.6 to -1.8V include vanadium(V/IV) and possibly vanadium (IV/III) species as well as the EDTA ion since voltammograms of these solutions show peaks in this range.

Figure 4.8.1 shows a cyclic voltammogram of an aqueous solution of $Cs[VO(O_2)EDTA]$ in 0.2M $LiClO_4$ ($\sim x10^{-3}$M). Three cycles are shown (curves 1, 2 and 3) and the starting potential is approximately 600mV. The initial scan was cathodic.

To compare the electrochemical behavior of this compound in aqueous solution with the electrochemistry of V(V) in analogous systems, voltammograms shown in figures 4.1.1 through 4.1.8 and 4.8.1 through 4.8.5 were taken.

From the cyclic voltammograms of the various systems, the plots of the peak potentials, and the potentiometric titration information, the following observations are made:

1) In 0.2M $LiClO_4$, the position of peaks on the voltammogram of the compound show some similarities

and differences to those present for the mixture of components. Also, some of the peaks present on these voltammograms are present on the voltammogram of free EDTA in 0.2M $LiClO_4$ (fig. 4.8.5), (i.e. near 1350 and -1480mV). A similar situation occurs in 0.2M H_2SO_4 (see fig. 4.8.2 and 4.8.4). In 0.2M H_2SO_4 the compound has very weak anodic peaks near 950 and 1330mV which match sharp peaks at these potentials on the voltammogram of the mixture of components but the similarity ends there.

This information indicates that the electroactive species formed upon dissolution of the compound in both 0.2M $LiClO_4$ and H_2SO_4 are not those that form upon mixing the components but the EDTA ligand has an important role in each.

2) The vanadium (V/IV) peaks near 50 and 200mV do not show a trend for the series of V(V), V(V) and H_2O_2, and V(V), H_2O_2, EDTA as was the case with the hydroxypolycarboxylato ligands. The Cs-salt does not show peaks in this area (see fig. 4.8.6).

3) The potentiometric titrations show good agreement in the stoichiometry and the reproducibility of the potentials measured at characteristic

points for the Cs-salt. The potassium salt behaved much differently (i.e. it never reached the potential of excess Ce^{4+}). The Cs-salts did not behave like the mixture of components in acid solutions. The K-salt showed some similarities to the acid solutions made by mixing components.

pH = 5.26 at the end of 40 cycles

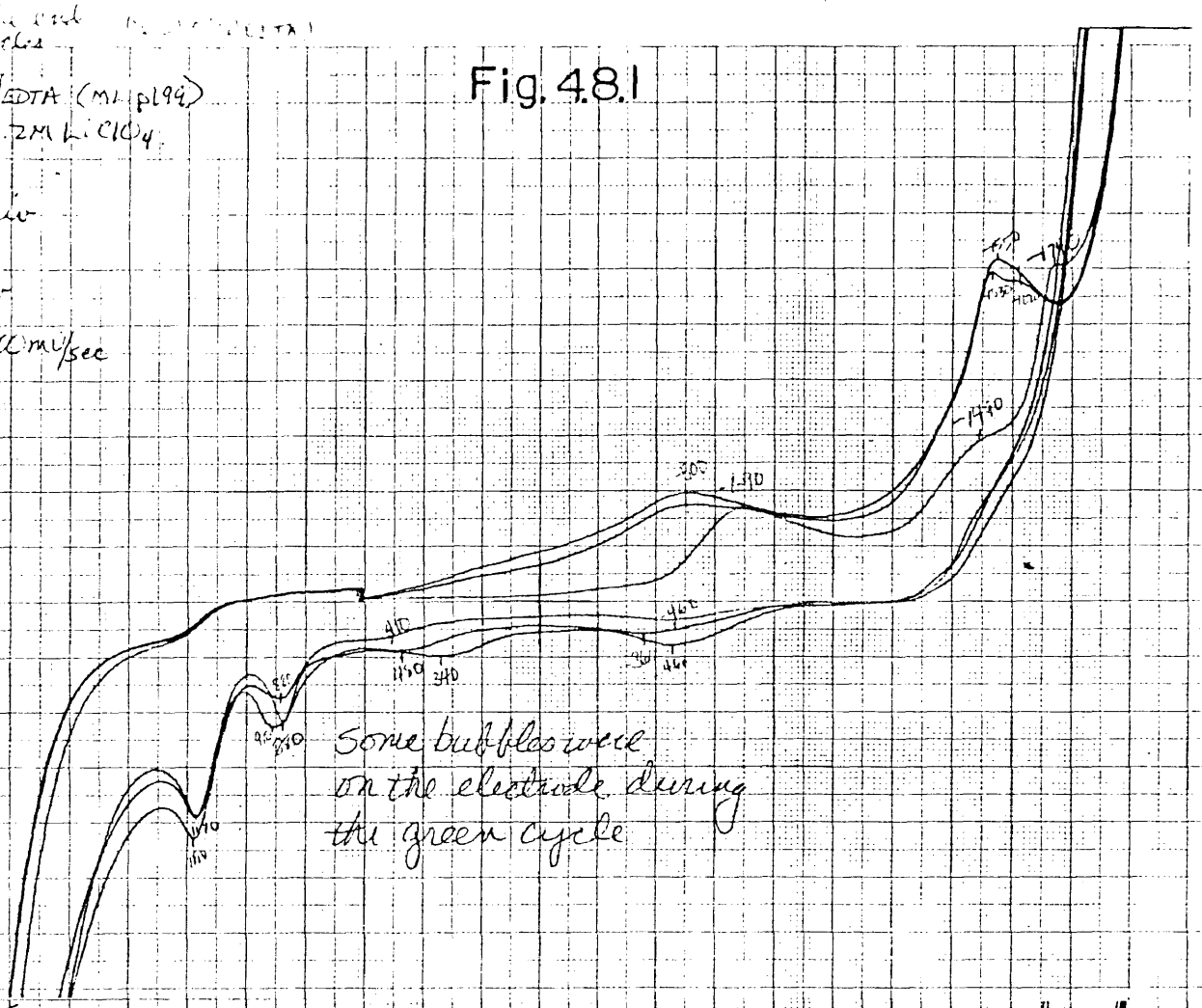
30 mg V/H2O4/EDTA (ML. P199) in 15 ml 0.2M LiClO4

x = 200 mv/div

y = 20 uA/div

Scan rate = 100 mv/sec

Fig. 4.8.1



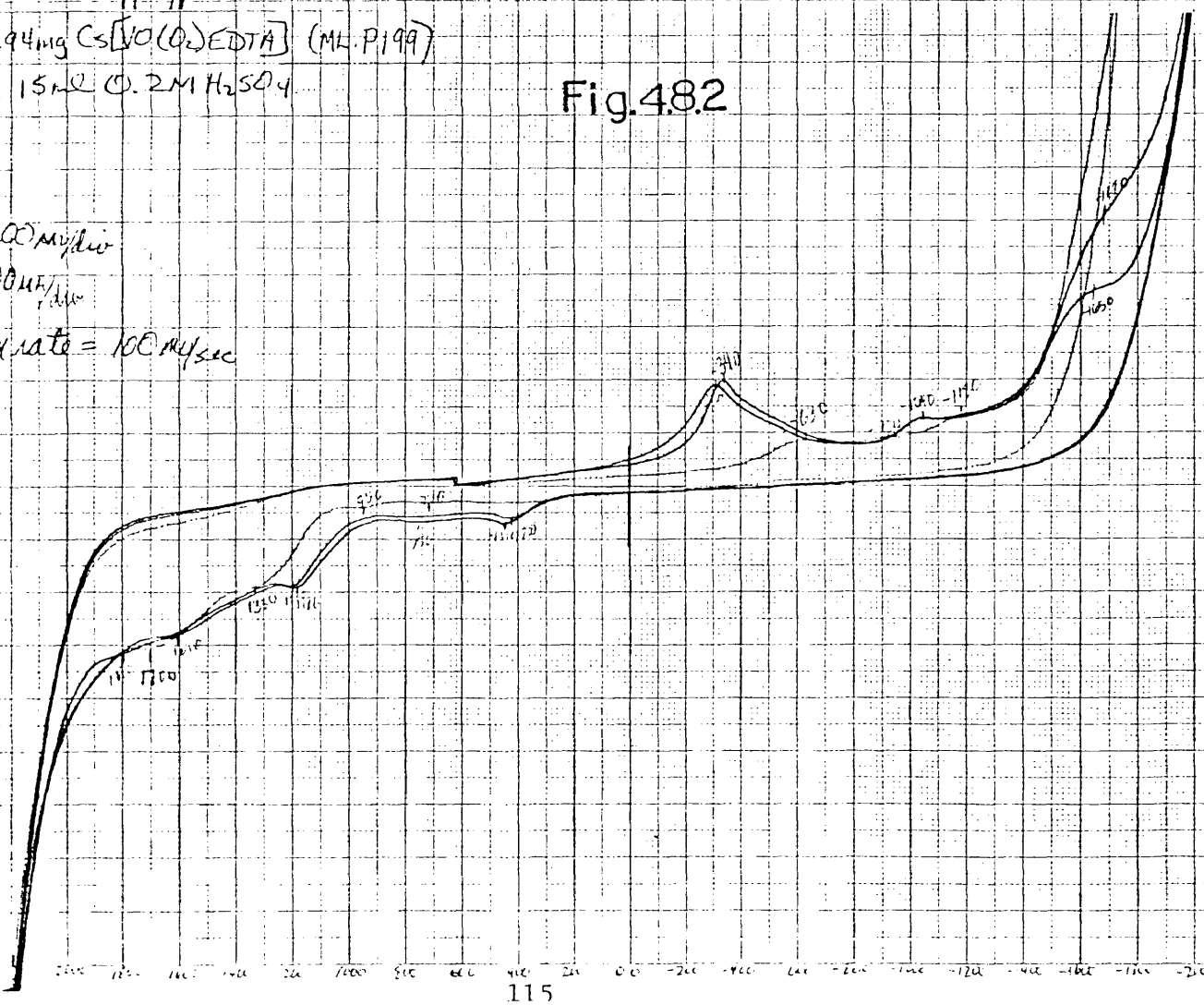
30.94 mg Cs[VO(O)EDTA] (ML. P199) in 15 ml 0.2M H_2SO_4

Fig. 4.8.2

x = 200 mv/div

y = 100 uA/div

Scan rate = 100 mv/sec



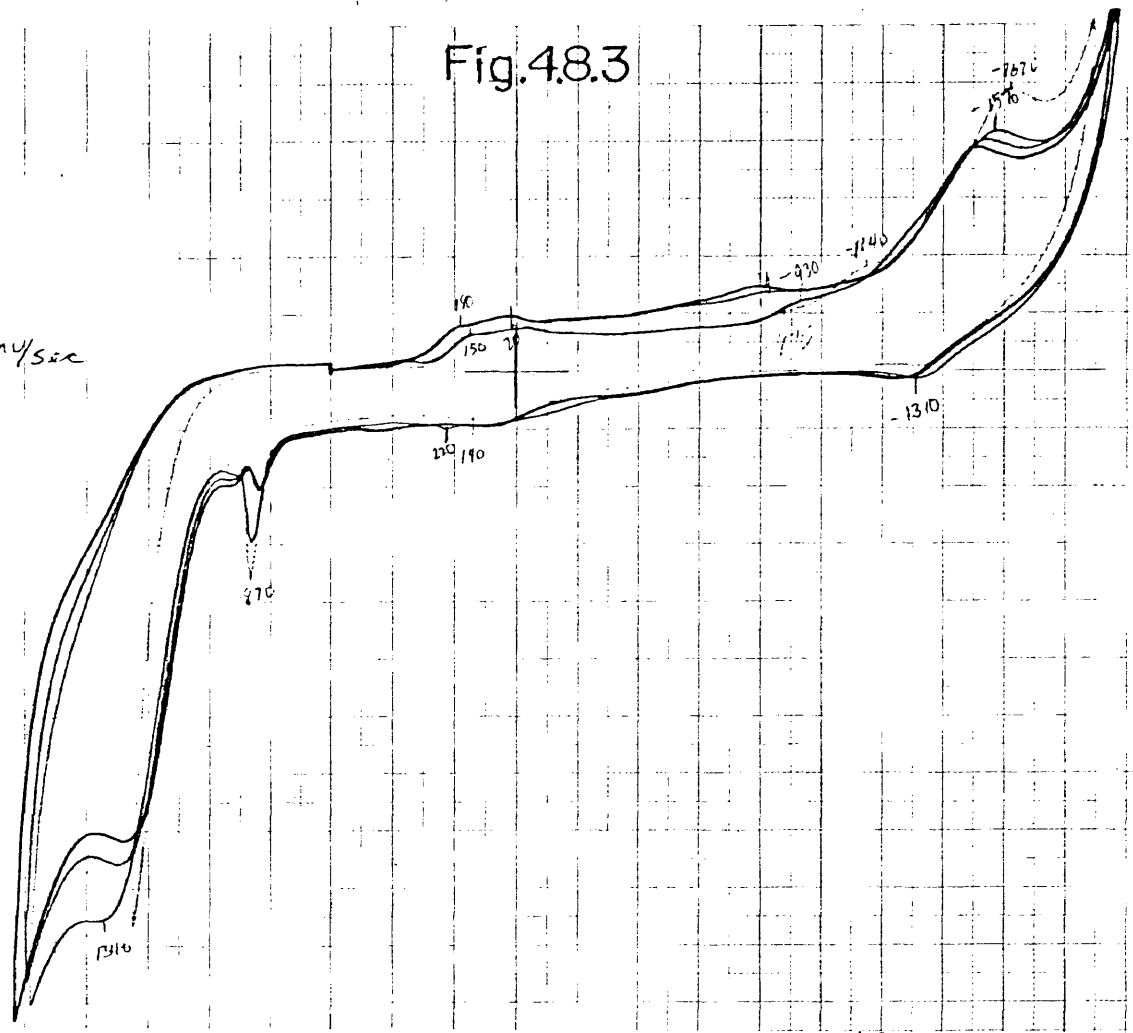
pH = 3.65
1.00×10^{-3}M VO^{2+}
1.08×10^{-3}M H_2C_2
2.0×10^{-3}M EDTA
0.2M $LiClO_4$

X = 200 mv/cm

Y = 10 μA/cm

Scan rate = 100 mv/sec

Fig. 4.8.3



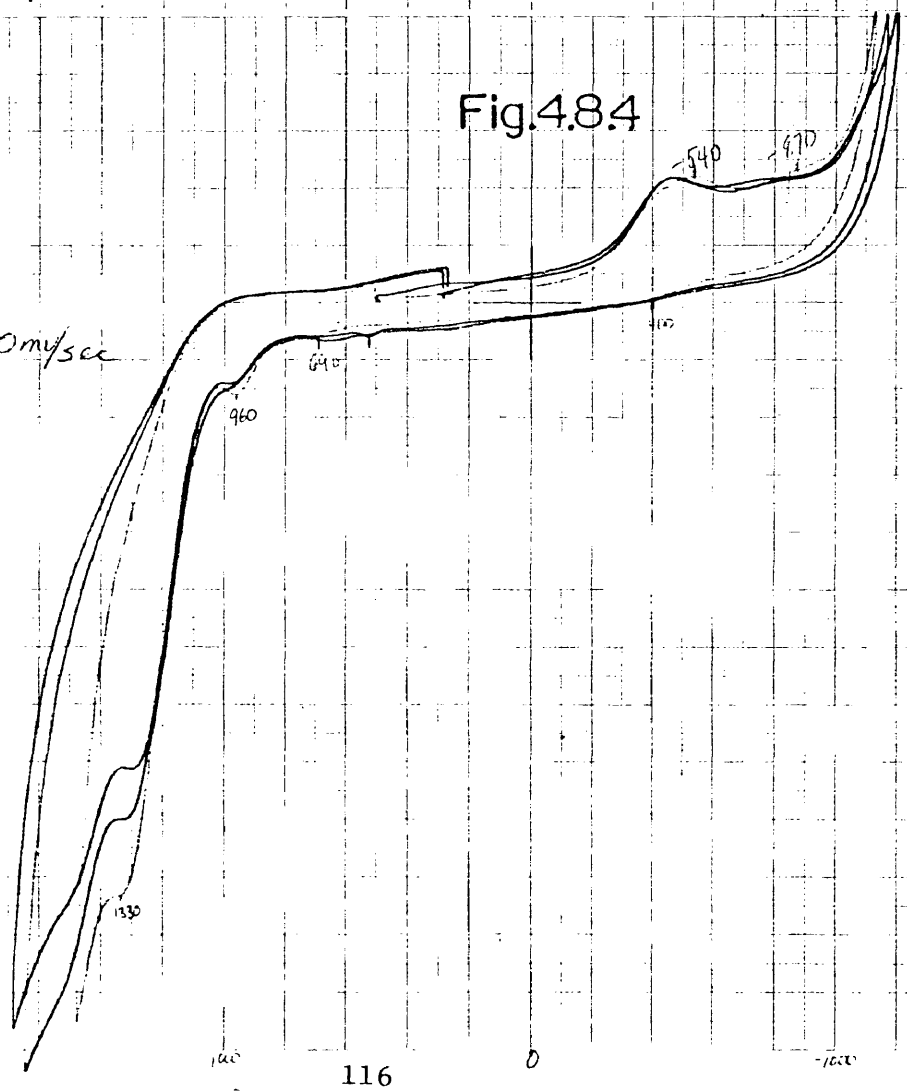
1.00×10^{-3}M VO^{2+}
1.08×10^{-3}M H_2C_2
2.0×10^{-3}M EDTA
0.2M H_2SO_4

X = 200 mv/cm

Y = 10 μA/cm

Scan rate = 100 mv/sec

Fig. 4.8.4



DJM P.129

pH=4.95

2.0×10^{-3}M EDTA

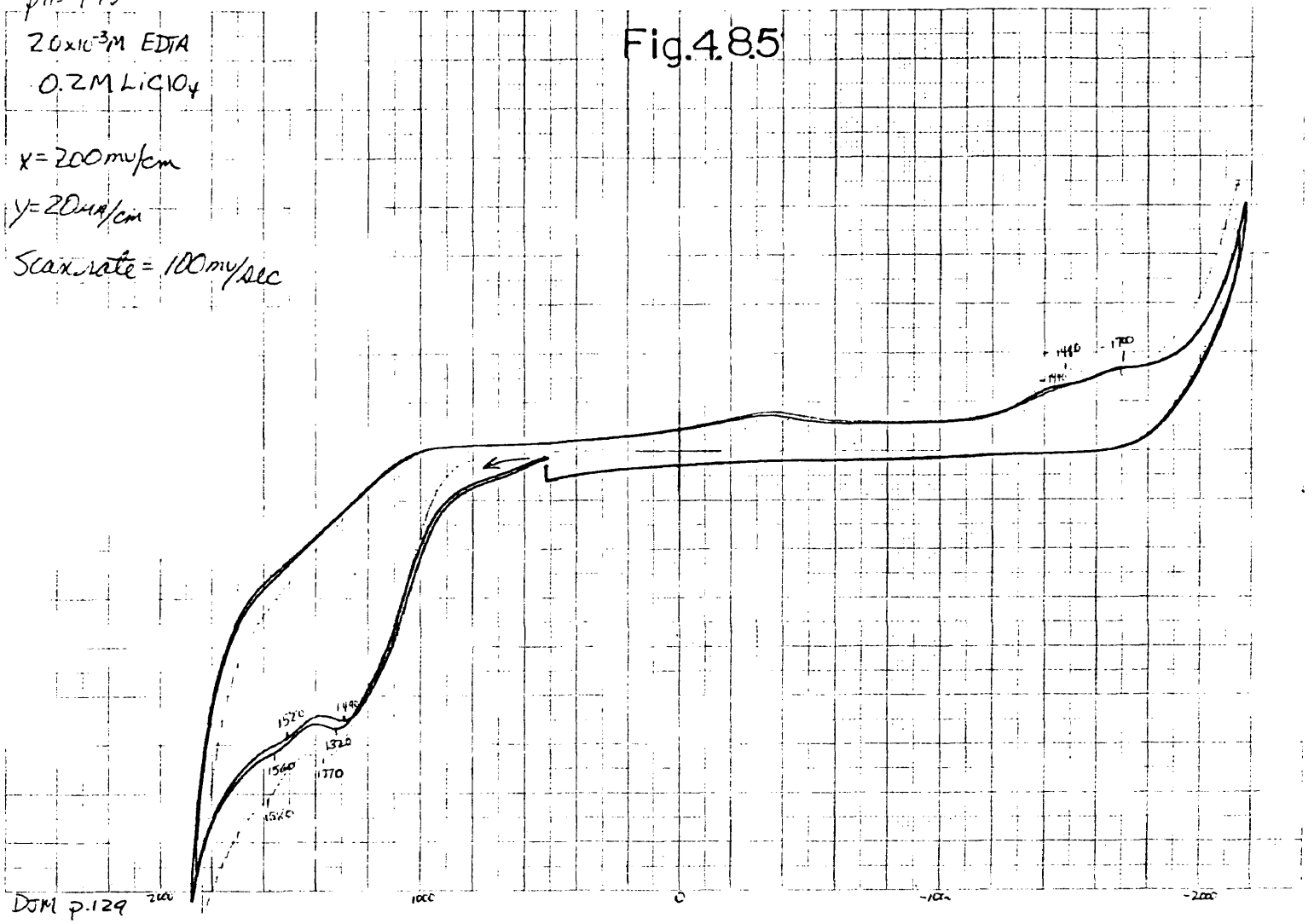
0.2M $LiClO_4$

x=200mv/cm

y=20μA/cm

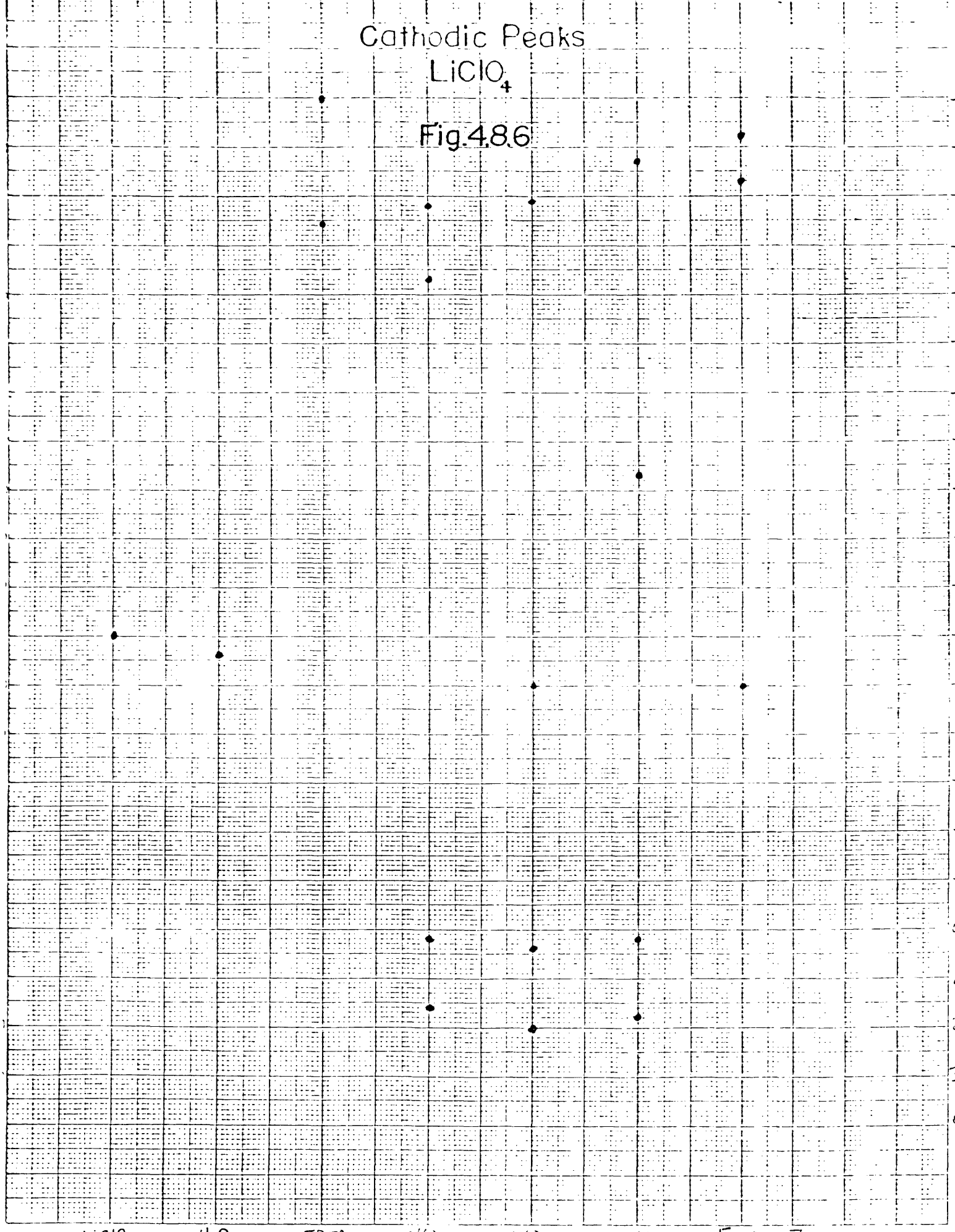
Scan rate = 100mv/sec

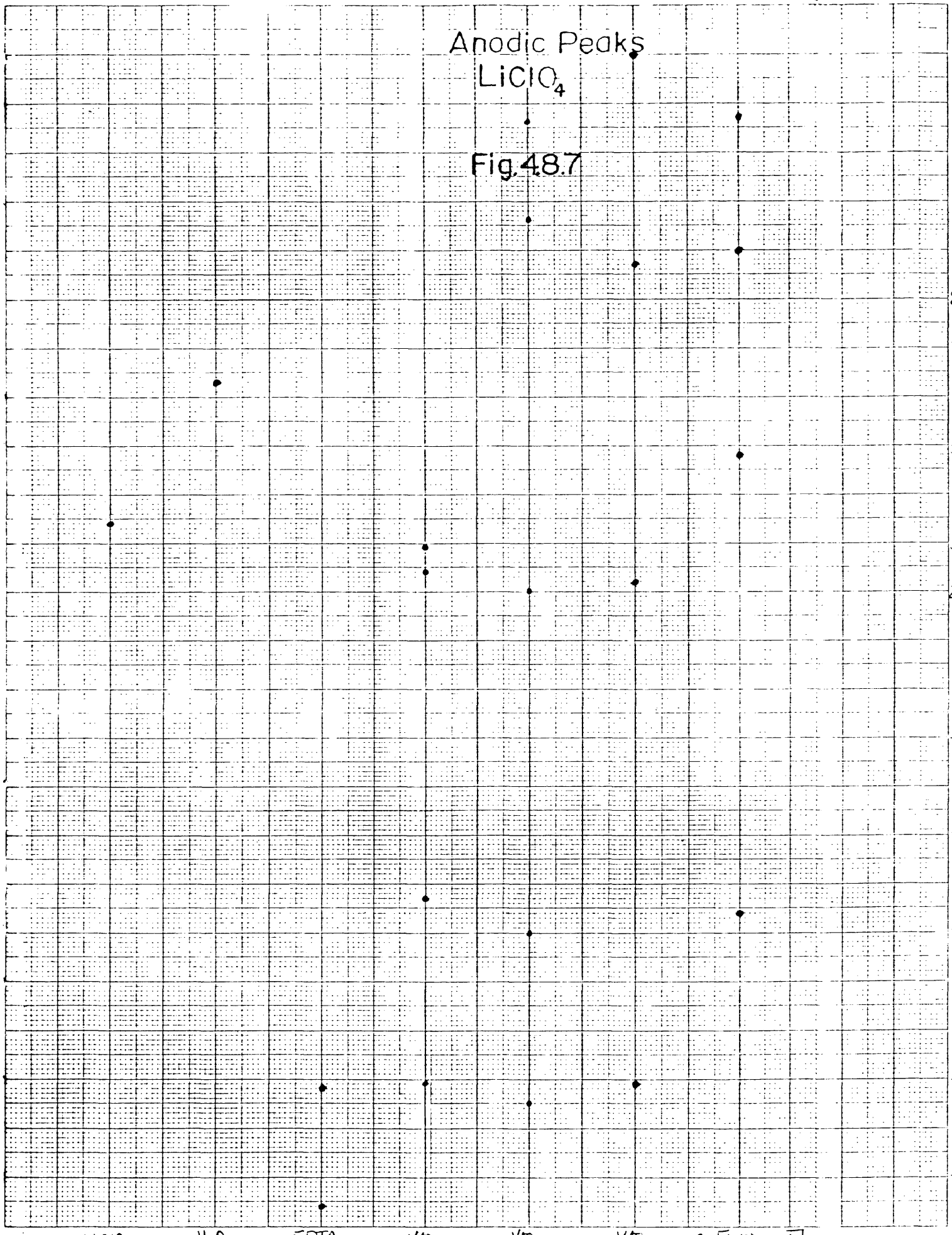
Fig.4.8.5

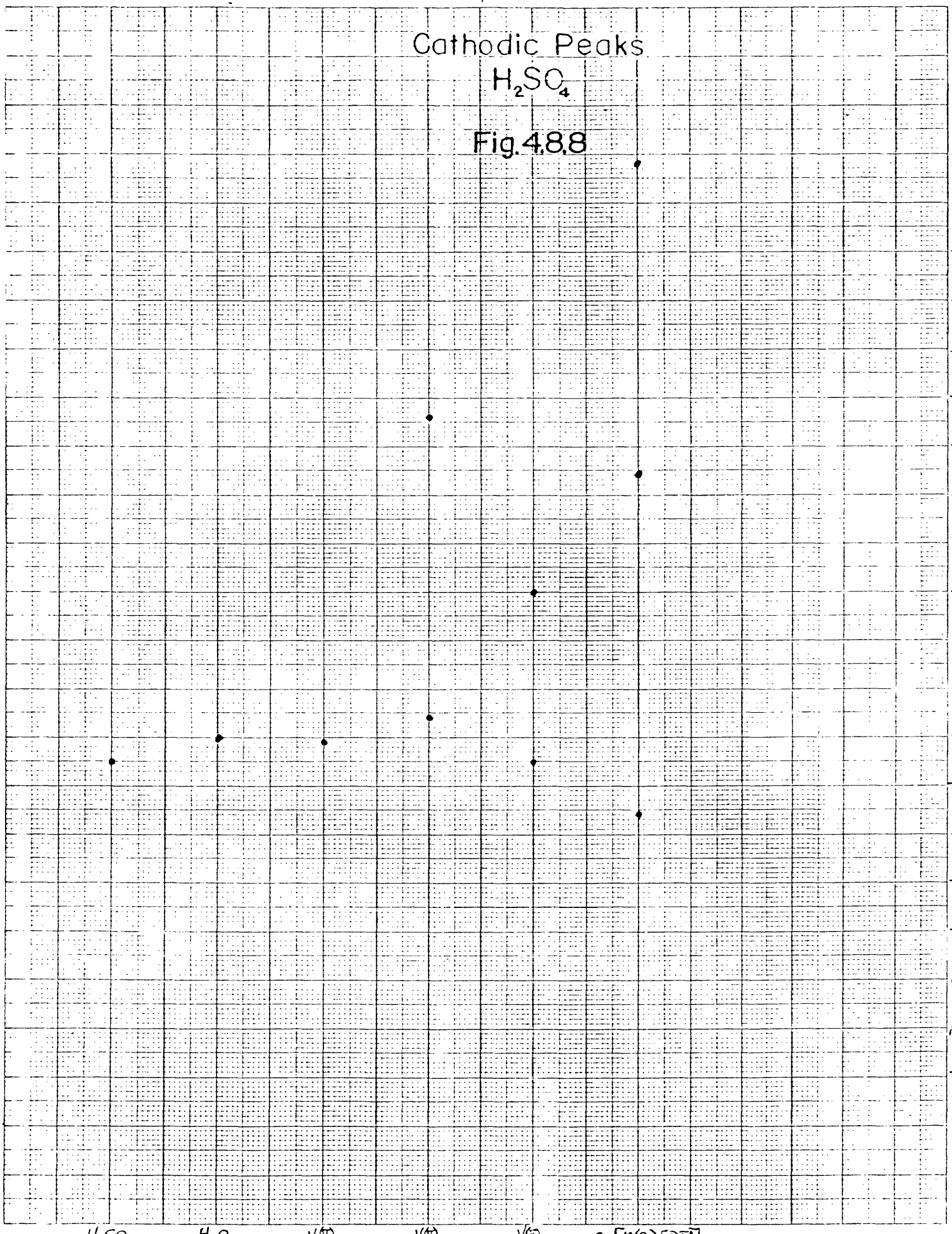


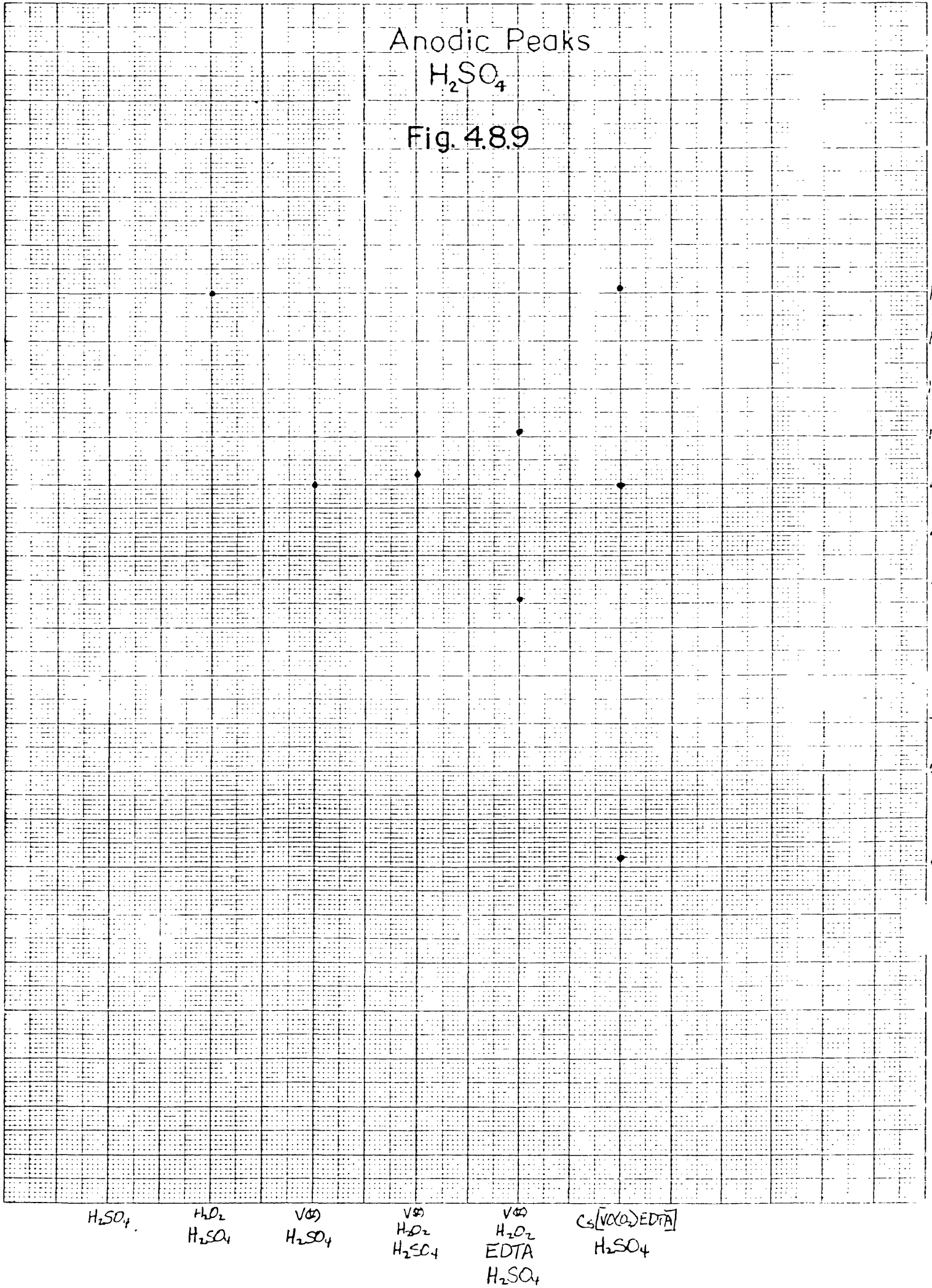
DJM p.129

5-24-74


Cathodic Peaks
$LiClO_4$
Fig.4.8.6
$LiClO_4$
H_2O_2 $LiClO_4$
EDTA $LiClO_4$
V(V) $LiClO_4$
V(V) H_2O_2 $LiClO_4$
V(V) H_2O_2 EDTA $LiClO_4$
Cs[VO(O$_2$)EDTA] $LiClO_4$


Anodic Peaks
LiClO4
Fig. 48.7
LiClO4
H2O2 LiClO4
EDTA LiClO4
V(V) LiClO4
V(V) H2O2 LiClO4
V(V) H2O2 EDTA LiClO4
Cs[VO(O2)EDTA] LiClO4


Cathodic Peaks
H_2SO_4
Fig. 4.8.8
H_2SO_4
H_2O_2 H_2SO_4
V(IV) H_2SO_4
V(IV) H_2O_2 H_2SO_4
V(V) H_2O_2 EDTA H_2SO_4
Cs[VO(O$_2$)EDTA] H_2SO_4


Anodic Peaks
H_2SO_4
Fig. 4.8.9
H_2SO_4
H_2O_2 H_2SO_4
V(V) H_2SO_4
V(V) H_2O_2 H_2SO_4
V(V) H_2O_2 EDTA H_2SO_4
$C_5[VO(O_2)EDTA]$ H_2SO_4

5. CONCLUSION

This thesis includes studies on the characterization of peroxo heteroligand complexes of vanadium(V) under different aqueous conditions. Two electrochemical methods were used: cyclic voltammetry and potentiometric titrations.

The following compounds have been investigated: $(NH_4)_4[O(VO(O_2)_2)_2]$; $M^I_3[VO(O_2)_2C_2O_4]$, M^I=K,NH_4; $M^I[VO(O_2)L]$, L=malate, citrate, tartrate, NTA and EDTA, M^I=K, NH_4, Cs. Electrochemical behavior of the aqueous solutions of these complexes at different acidities was compared to the behavior of the mixture of the respective components under identical conditions.

Potentiometric titrations served to determine the stoichiometry of peroxide oxidations in a varied time span and to measure the potential at some critical points of the titration. It has been observed that some ligands change the course of the potential during the addition of strong oxidants such as Ce(IV), MnO_4^- and $Cr_2O_7^{2-}$. Cyclic voltammetry was used to determine the number of electroactive cathodic and anodic species as well as the potentials at which they are reduced or oxidized on the glassy carbon electrode.

Results obtained from the cyclic voltammograms show that all the V(V) peroxo heteroligand systems behave irreversibly and that the number and potentials of the electroactive species depend upon the heteroligand and the pH. Overall, there is a significant difference in the electrochemical behavior of complexes in the neutral electrolyte $LiClO_4$ and in the acid solutions studied. The complex species present in these systems must therefore vary from one system to another.

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